



**SWEDISH GEOTECHNICAL INSTITUTE**

**PROCEEDINGS**

**No. 26**

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**ORGANIC MATTER IN SWEDISH CLAYS  
AND ITS IMPORTANCE FOR  
QUICK CLAY FORMATION**

**By  
Rolf Söderblom**

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**STOCKHOLM 1974**





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## PREFACE

In a previous report from the Institute on quick clay (Proceedings No. 22, 1969), salt in Swedish clays and its importance for quick clay formation has been investigated. The background of the quick clay research at the Institute - mainly the slope stability conditions in the Göta River Valley in south-western Sweden - was reviewed briefly in the preface of this publication.

In March 1974 a second report on the quick clay topic was published with the title "New Lines in the Quick Clay Research" (in the Institute's series Reprints and Preliminary Reports, No. 55). It consists of three papers and presents, e.g., the so called "rapidity number", an index of the work required to break down the structure of a clay. A new definition of quick clay has also been suggested. Further, the application of a remote sensing method in the quick clay research is described. The possible role of leaking sewage lines in the ground and the risks of a reduction of the strength properties when sewage infiltrates the soils have been stressed.

The present work should be regarded as a complement to the salt studies described in 1969. The report deals mainly with organic materials in soils and its importance for the formation of quick clays. The natural dispersing substances which are very common in Swedish soils and may contribute to the high sensitivity of clays have especially been investigated. It is also stated that many of the chemical processes going on in the ground and which affect the soil properties are due to human activity. It is necessary to control these processes more in the future. With the present report the Institute's contribution to the basic research on the quick clay problem - a work that started already in 1955 - is terminated. It should, however, only be considered as a beginning and much work still remains before a complete picture of the quick clay problem has been obtained. Slides where quick clay plays an important role will probably occur in the future. Further research will undoubtedly be needed. Increased knowledge of the importance of the ground water in this connection will be required.

The research work has been planned and directed by Mr R. Söderblom, who also prepared the report. Parts of the laboratory investigations have been made by Mrs I. Almstedt. The work has been carried out at the Research and Consulting Department A of the Institute with Mr G. Lindskog as head in co-operation with Professor A. Ölander, of the Physico-Chemical Department at the University of Stockholm. It has been supported by grants from the Swedish Board for Technical Research, the Swedish Natural Science Research Council and the Swedish Council for Building Research.

The report has been edited by Mr N. Flodin and Mr O. Holmquist of the Technical Secretariat, at the Institute.

Stockholm, April 1974

SWEDISH GEOTECHNICAL INSTITUTE



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## SUMMARY

This report deals with the importance of, primarily, organic matter in Swedish quick clays. Particularly, the relationship between dispersing agents and sensitivity has been investigated.

A study of a great number of reports in the SGI files showed that varved, fresh-water sedimented quick clays are relatively common in Sweden.

The adsorbed double layer as well as the Donnan effect and the chemical equilibrium between double layer composition and pore water composition is discussed. The possibility that organic matter can form a fissured structure in the clay is also treated.

Methods have been developed to isolate dispersing agents from Swedish clays and attempts made to analyse these agents. It is found that it is easy to isolate dispersing substances but very difficult to find substances with a known composition. Especially the humic acids are impossible to analyse at present.

One group of dispersing substances which can be isolated, purified and chromatographed is the soaps. These are occurring in series of both saturated and unsaturated fatty acids. Another group that can be detected comprises the tensides.

It has also been shown that dispersing agents isolated from quick clay can originate from impurities infiltrated in the ground.

## 1. INTRODUCTION

It has long been known that an excess of water locally in a slope can affect its stability and in extreme cases lead to landslides. However, it has also been shown that the susceptibility of a specific area to failure is often not predictable when based on usual soil engineering considerations (Mitchell & Woodward, 1973). In recent years it has been found that in this respect soil chemistry also plays an important role. Especially important is the quantity of dissolved sodium cations in the pore water relative to the quantities of other main basic cations (calcium and magnesium), Sherard, Decker & Ryker (1972).

Analyses from the more important slides in Sweden in recent years have indicated that they have always occurred in clay soils having sodium as dominating cation in their pore water. These types of soils as a rule exist very locally. Söderblom (1969) has shown that a clay with sodium as dominating cation in the pore water can only develop from a natural clay system when calcium and magnesium depressing agents (dispersing agents) are present. In most cases Swedish clays of this type have the property of being quick.

It has been suspected that processes are going on in nature successively changing the clay system from a calcium magnesium system to a sodium system. The further details of these processes have so far been unknown. It has been suggested that this sodium excess has occurred from a leaching of a clay system precipitated in sea water, but the Donnan condition indicates that this cannot be the case. Dispersing agents must be present to explain the observed sodium excess.

As far as the present Author knows no systematic investigation has been carried out to prove whether dispersing agents exist in nature or not and whether substances of this kind can have an influence in the processes changing the clay properties. This is of importance to the long-term stability conditions of a

slope. Before any further discussion of the in situ processes transforming clays into unstable quick clays is made, it seems necessary therefore to investigate in more detail the importance of dispersing agents in nature. One practical way seemed to be to isolate any dispersing agents that might occur and to analyse them. In reality, however, the problem proved to be much more complicated than expected and a new approach was required.

In connection with studies of recent large landslides it was possible to localize sources of infiltrated water and obtain an understanding of the infiltration processes which are involved in the successive clay changes. It was found that, e.g., dispersing agents of both natural and artificial origin occur in the processes.

In this report a systematic isolation and analysis of mainly organic dispersing agents from clays of different types will be treated.

The localization of the test sites is given on the maps in App. 1 and 2 and in the table in App. 3, where some basic data also are presented.

### 1.1 Brief Review of the Swedish Geotechnical Institute's Work on the Quick Clay Problem

The present investigation began in 1955 and was intended to explain certain peculiarities in shear strength in a clay profile at Enköping (Jakobson, 1954) by means of the Norwegian salt leaching theory (Rosenqvist, 1955). In this connection the question of factors influencing the sensitivity also became urgent. The first experiments (Enköping and Marsta) showed a good agreement between the salt leaching theory and the shape of the sensitivity curve in situ (Söderblom, 1957).

On a parallel basis an extensive investigation was

conducted by, e.g., the Swedish Geotechnical Institute in the Göta River Valley, where two large landslides had recently occurred (Surte in 1950 and Göta in 1957). A great number of samples were available and it was very soon found that there could not be a direct relation between the salt content of marine sediments and their quickness. In many cases completely leached sediments were found to have a low sensitivity. Some processes for forming high sensitivity - other than leaching - must be present. It was well known (Rosenqvist, 1946) that almost all clays could be made quick by dialysing them in certain solutions of so called dispersing agents, e.g. sodium pyrophosphate.

The Author suggested that clay dispersing processes of this kind must occur in nature. Therefore studies were made to try to isolate dispersing substances from natural quick clays. The first type isolated was carbonate which was found in a quick clay from "Gärdet", an area in Stockholm (Söderblom, 1959).

At the same time the Geotechnical Department of the Swedish State Railways stated that typical fresh-water clay sediments could be quick and that they had no content of carbonates. One place with such sediments was in the vicinity of the former railway station at Rosshyttan. It was found that these quick clays occurred in connection with peat. Analyses showed that the natural humic salts were strong dispersing agents able to transform normal clay into quick clay. Here the Author started investigations aimed at isolating dispersing agents from quick clay and peat (Söderblom, 1960).

In 1961 the Swedish State Railways reported that clay samples, especially of quick clay, showed a change in sensitivity after some time of storage, i.e. ageing effects occurred (Jerbo, Norder & Sandegren, 1961). This effect, which indicates instability in the quick clay system, is impossible to refer to the salt leaching theory. The ageing effect was further studied by the Author who found that it was accompanied by changes in the chemical composition of the pore water, directly indicating the importance of instable calcium-magnesium depressing agents (dispersing agents).

From the results obtained, the question arose whether it was possible to isolate quick clay forming substances from natural quick clays in general and to analyse them. Systematic work was started to isolate different dispersing agents, especially from marine quick clays in the Göta River Valley but these substances proved to be more complicated than expected. (Some results were published, Söderblom, 1966.) Supplementary tests have been made successively and the original work including some additional results is presented in this report.

At the same time papers were published on the difference between pore water composition in leached non-quick clays and leached quick clays (Penner, 1965; Talme et al., 1966). It was stated that quick clays and non-quick clays could have the same total salt content but that the ionic composition differed in such a way that quick clays had sodium as the dominating cation in their pore water, whereas normal clays have calcium and magnesium. It was stated that quick clays and normal clays could exist side by side in the same sedimentation area. No valid explanation of these peculiar conditions was put forward by the authors. It was, however, mentioned that salt leaching was decisive for the conditions.

At the same time the Author's studies in physical-chemistry at the University of Stockholm directed attention to the Donnan effect. It was easy to conclude that a leaching according to Rosenqvist must lead to a system with calcium and magnesium as dominating cations. This is due to much stronger electrostatic adsorbing forces of the divalent ions than of the monovalent ions.

For this reason it was decided that an investigation of salt and its influence on the geotechnical properties should be made without any suppositions. This investigation (Söderblom, 1969) indicated clearly the importance of organic material in the repressing of the Donnan conditions. No explanation was, however, obtained of the fact that quick clays appear so locally in normal clays.

After that it was also noticed that the standard definition of quick clay includes materials with quite different properties. Studies in this connection

resulted in the introduction of the concept "rapidity number" (Söderblom, 1973). At the same time it was observed that the rapid quick clays<sup>1)</sup> were found in the vicinity of local ground water arteries and that the quick clay problem to some extent was a ground water problem as well as an infiltration problem. It was found that in areas with hard ground water no quick clay can be formed. Details of this work are further presented by Söderblom (1974).

It was possible in the above mentioned investigation to develop a special method based on remote sensing in the VHF-band to localize water arteries and infiltration sources. Thereafter it was easy to get information on the composition of the infiltration water. After that it was possible to initiate a study of the influence of the infiltrated water on the clay. It was found that in many cases the soft water environment causing the local quick clay formations with deviation in pore water composition originated from an infiltration of sewage in ground water arteries. The investigations directed the quick clay problem to the chemistry of the disposal of wastes in soil and to the problem of pollution of ground water related to soil properties.

In this connection it should be mentioned that human activity is not the sole source in changing the ground conditions which are necessary to transform an originally stable clay soil into unstable quick clay.

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1) A rapid quick clay requires a small amount of work to be broken down.

Studies of the quick clay problem from different points of view have also been made by the late Professor Justus Osterman of the Swedish Geotechnical Institute (Osterman, 1963). In another paper (Osterman, 1960) dealing with the stability of clay slopes he points, e.g., to the low strength values close to permeable layers in clay.

Kallstenius (1963) showed that Swedish quick clays have a fissured structure. This fact has later been confirmed in the case of Canadian quick clays (Eden & Mitchell, 1970). In the present paper this problem is treated further.

To fully complete this brief review it should also be mentioned that Pusch (1966) started his investigations on the micro-structure of quick clay. Pusch & Arnold (1969) published results from some tests performed earlier at the Institute to verify the salt leaching theory by experiments on organic-free illitic clay but obtained negative results.

The importance of dispersing agents has been illustrated from investigations of several landslides (Söderblom, 1973 and 1974). The most obvious slide in this respect occurred in 1972 in connection with a broken pressure pipe for waste water, placed in an infiltration zone (Söderblom, 1974). Dispersing agents were spread into a large area. This points on the practical and economical side of the problem.

## 2. GENERAL CONSIDERATIONS AND BASIC TERMS

### 2.1 Definitions

Some definitions given in earlier publications (Söderblom, 1969 and 1974) will not be repeated here, but some supplementary facts will be given.

H<sub>1</sub>-value (relative strength number of remoulded sample) is, as found by Jerbo (1967), not a material constant. Different H<sub>1</sub>-values are obtained if one

remoulds the clay in air or in an inert atmosphere or, as done by Jerbo, in "airproof" conditions. This may be due to the instability of the organic matter. The H<sub>1</sub>-value of a clay as a rule shows ageing effects, i.e. changes with time. Thus, this value has, in fact, another meaning than that adopted by the Swedish State Railways Geotechnical Commission (1922).

H<sub>3</sub>-value (relative strength number of "undisturbed"

sample). It is proved that this value is dependent on the sampling and testing conditions. It is, as is also the case with the  $H_1$ -value, strongly time dependent, i. e. the samples are affected by ageing. Due to the instability of certain organic constituents in the clay (cf. Ch. 7.3.4) it is certain that it is not permitted to make conversions of  $H_3$ -values determined on samples transported to the laboratory into shear strength in situ.

Sensitivity ( $H_3/H_1 = S_t$ ). The uncertainty described above concerning the  $H_1$  and  $H_3$ -values will naturally be reflected in H-quotient. It should also be observed that the sensitivity determined in situ frequently differs from that determined in extracted samples.

Quick clay. The Swedish term "kvik" <sup>\*)</sup> originates from the old Nordic word "queck" = living. It was originally attributed to a material being fluent for only a very little affection (cf. Reusch, 1901). After the fall-cone method was developed (in the 1920's), it became possible to propose a mathematical definition of the concept quick clay but, unfortunately, the term quick clay changed its meaning. The modern definitions characterize all materials with a high sensitivity (generally  $S_t = H_3/H_1 > 50$ ) as quick clay independent of remoulding work. This is not in accordance with the original meaning of quick clay. It seems more proper to state that a quick clay shall also have a minimum rapidity value  $R_n \geq 8$  as suggested by Söderblom (1974).

Rapidity number ( $R_n$ ) is an index of the remoulding work required to break down a quick clay completely. At present the test is roughly carried out in a Casagrande liquid limit apparatus. The sample is allowed to drop 1 cm 250 times. The more the sample is affected, the higher the rapidity number. The scale is graduated from 1 to 10 (Söderblom, 1974).

## 2.2 Scope of Investigation

As mentioned in the introduction relatively complicated colloid chemical reactions are associated with the quick clay forming process. It was also stated

\*) English "quick"

that organic materials of different types play an important part in the formation of the high sensitivity and the observed fissured structure of quick clays.

Because of the great variety of organic materials (natural and those created by human activity) and their different influence on the properties of the clays, it has been necessary to limit this investigation to two main types of organic substances with completely different action, viz. gels with cementing stabilizing effects and the more low molecular organic substances having  $Ca^{2+}$   $Mg^{2+}$ -binding properties and being strong dispersing agents able to transform "normal" clays into high sensitive clays. But all intermediate forms exist and the different organic substances can be transformed into each other by chemical or by microbial means.

In the present report, the following items are treated:

- 1) Quick clay distribution in marine (salt-water) deposits and in fresh-water deposits.
- 2) The adsorbed double layer, the Donnan effect, the inhomogeneous ion distribution of high sensitive clays and their importance to the formation of quick clay and its strength properties.
- 3) A discussion of possible dispersing and cementing agents expected to exist in nature (formed either by natural processes or as a result of human activity).
- 4) Experiments with different types of dispersing agents and attempts to prepare synthetic quick clays having a fissured pattern similar to that occurring in nature.
- 5) Attempts to isolate substances with dispersing properties from different types of quick clays and to obtain an idea of their composition.

## 2.3 The Adsorbed Double Layer and its Importance to Quick Clays

In preceding papers by the present Author no consideration has been taken to the adsorbed double layer of the quick clay particles. The double layer



theory and ion exchange in connection with clays and quick clays has been discussed by several authors, e.g. Rosenqvist (1955); Lambe (1958); Tullström (1961); Marshall (1964); van Olphen (1965); Penner (1965) and Moum et al. (1971). The works by Moum and Tullström illustrate that it seems impossible to obtain any differences in the amount of the ionic composition of the adsorbed cations between high sensitive clays (quick clays) and salt-free clays with low sensitivity (normal clays). As will be seen in Ch. 4.1 of this report, it has not been possible to find any relation between the ionic composition in the adsorbed double layer and the sensitivity of a clay.

### 2.3.1 The Donnan Effect

If a clay sample is dialysed as described by Söderblom (1969) and the process is allowed to reach a state of equilibrium, one might expect that the concentration of dissolved substances would be almost the same inside and outside the dialysis membrane. But this applies only to non-electrolytes. If the colloid contains electrically charged atom groups as is the case for clays, low molecular electrolytes will get quite different concentrations inside and outside the clay sample. These electrolyte distributions are called the Donnan equilibrium.

Donnan & Harris (1911) made dialysis experiments on Congo red in water being analogous to the experiments to verify the salt leaching theory. Congo red is a negatively charged colloid, as is clay and Donnan's reasoning can be applied unchanged to clays.

Because of the complicated charge distribution in a colloid, it is not practical to speak about the concentration of the colloid. Instead, one can use the conception normality ( $n$ ).

By dialysing experiments Donnan and Harris obtained the following results when working with pure Congo red and sodium chloride. After equilibrium the ionic concentration in the outer dialysing solution was  $c_{Na}^+ = c_{Cl}^-$ . Depending on the electron neutrality the concentrations in the inner solution must be

$$c_{Na}^+ = c_{Cl}^- + n_{Ko^-} \quad (1)$$

At the equilibrium the chemical potential and the activity of NaCl must be equal in both phases; thus

$$a_{NaCl}^i = a_{NaCl}^o \quad (2)$$

If the activity factors are not taken into consideration this can be written

$$(c_{Cl}^- + n_{Ko^-}) \cdot c_{Cl}^- = (c^o)^2 \quad (3)$$

When the salt concentration is small in comparison to the amount of colloid,  $n_{Ko^-}$ ,  $c_{Cl}^-$  must be less than  $c_{Cl}^o$ . From a colloid containing NaCl, the  $Cl^-$  ions could be leached very effectively because their concentration in the colloid at equilibrium will decrease far below the concentration in the outer solution. On the contrary, the  $Na^+$  ions will only be partly leached and their concentration will remain greater than in the outer solution.

If, on the other hand, the concentration is large in comparison with  $n_{Ko^-}$ , the chloride ions have almost the same concentration in both the solutions. The Donnan effect thus fades away in concentrated salt solutions.

In the general case when the salt has the formula  $A_p B_q$  and the ions have the charges  $z_+$  and  $z_-$ , the equation will be

$$\begin{aligned} (p c_B^i / q + n_{Ko^-} / z_+)^p \cdot (c_B^i)^q &= \\ &= (c_A^o)^p \cdot (c_B^o)^q \end{aligned} \quad (4)$$

Also in this case an uneven salt distribution is obtained when the concentration is small.

In the case of several types of ions being present it is still valid that a salt which forms with one kind of anions, shall have the same activity in the two solutions

$$(a_A^i)^p \cdot (a_B^i)^q = (a_A^o)^p \cdot (a_B^o)^q \quad (5)$$

$$(a_A^i / a_A^o)^p = (a_B^o / a_B^i)^q \quad (6)$$

If both members are raised to  $1/pz_+ = 1/q |z_-|$  is obtained

$$(a_A^i/a_A^o)^{1/z_+} = (a_B^o/a_B^i)^{1/|z_-|} \quad (7)$$

hence

$$(a_A^i/a_A^o)^{1/z_+} = (a_B^i/a_B^o)^{1/z_-} \quad (8)$$

When the cation A is linked together with another kind of anion and the anion with another kind of cation, it is found that this function will have the same value for all mobile ions

$$K = (a^i/a^o)^{1/z} = (c^i/c^o)^{1/z} \quad (9)$$

when  $z$  is negative for the anions.  $K$  is thus the distribution factor for the monovalent ions,  $K^2$  for the divalent ions, etc.

When all ions in the system have the same valency, it is possible to obtain a simple expression for the distribution factor

$$K^{|z|} = 1 + n_{KO^-} / (\sum n_B^i + \sum n^o) \quad (10)$$

When the total amount of salt is great, all ions will be distributed almost equally in the inner and outer solutions, also those occurring in small amounts.

In the case of the negative colloid containing a small amount of ions, the value obtains a great value. When the outer solution contains small amounts of monovalent and divalent ions, the divalent ions will at equilibrium be accumulated as counterions in the colloid because their distribution factor is the square of that of the monovalent ions. When a colloid containing both divalent and monovalent ions is dialysed (leached), the monovalent ions will more easily leave the system and an enrichment of divalent ions will result. This is a very important fact in understanding of the natural leaching of clays.

The Donnan effect also causes that, when the electrolyte concentration is not too high, the squeezed pore water from a clay will get another salt content and another ionic composition than the solution in equilibrium with the clay particles (i. e. the pore water in its original state). The composition and salt content of the squeezed pore water is also dependent on the amount of water squeezed out, (cf. Kemper, 1960).

The Donnan effect is sometimes called negative adsorption, because in a negatively charged colloid system like clay, the negative ions are repelled from the system. The concept of negative adsorption is e. g. used in the equations for diffusion in a charged colloid system.

For further details of the Donnan effect see any good textbook in physical chemistry.

### 2.3.2 Syneresis in Clay Gels

Syneresis is the spontaneous expulsion of the liquid from a gel. It is a kind of internal dehydration (or desolvation) connected with shrinking. The phenomenon was treated scientifically already by Graham (1864). Syneresis occurs during the ageing of unstable gels as well as when slightly soluble substances are precipitated in a gel. It is often observed in extracted quick clay samples with a high rapidity number.

Shemyakin (1958) found that precipitation of  $HgCO_3^*$  or  $Ag_3AsO_4$  in gelatin or agar at certain concentrations causes spiral cracks, accompanied by syneresis of the gel. Diffusion of  $K_2CO_3$  in gelatin produces the same phenomenon which is called rhythmic forced syneresis.

Dobrolvol'skii (1964) stated that quaternary sediments in the tundra were aged naturally and that shrinkage accompanied with syneresis cracks had taken place in contact with a peat bog. Probably the precipitation of humic substances in the clay causes syneresis and results in cracks according to the theory of precipitation of a gel in a gel.

Eden & Mitchell (1970) found a network of micro-fissures in Canadian quick clay. Kallstenius (1963) made similar observations for quick clay from Vesten in the Göta River Valley and associated this, without any further explanation, with syneresis.

As will be seen later in this report, the precipitation of humus in the clay gel may be one of the factors causing these fissures.

\*) For interpretation of chemical formulas see e. g. Handbook of Chemistry and Physics.

### 2.3.3 Melanoidin - a Type of Laboratory-Prepared Humus

It is possible to prepare condensation products between amino acids and aldehydes, e.g. reducing sugars, having equivalent weight, molecular weight, elementary composition and active groups similar to those occurring in natural humic acids. Enders (1938) made such products by boiling a solution containing glucose and glycocoll. Schuffelen & Bolt (1950) used methyl glyoxal and glycocoll and obtained a product containing 2-3 % fulvic acids, 70-80 % hyalomelanic acids and 5-7 % humic acids.

These products are, however, of non-aromatic character and must, according to Kononova (1961), be considered only as very simplified models for natural humic acids. It is, of course, also possible to build up more complicated condensation products having aromatic parts, e.g. from polyphenols and amino acids.

The humic-like melanoidin is, as will be seen later in this report, very suitable when studying the structure formed by precipitation of humic substances in clay gels.

## 3. OBSERVATIONS OF FACTS IN CONNECTION WITH QUICK CLAY FORMING PROCESSES

### 3.1 General

Quick clays (in the simplified meaning of high sensitive clays) are, as stated by many authors, expected to be found only in marine clay sediments with a flocculated structure. In Sweden such clays occur e.g. in the Göta River Valley. These flocculated clays have another appearance than the varved clays which have distinct transitions between summer and winter varves. Clays of the later type are by most geologists considered to be sedimented in water with low salinity (fresh-water).

In recent years many deposits of varved quick clays sedimented in fresh-water have been found. These quick clays are frequently situated below a layer of peat (Newland & Allely, 1955; Söderblom, 1960; Jerbo & Hall, 1961 and Keinonen, 1963).

Keinonen found that Finnish Ancyclus clay was quick. He quotes several results from diatom analyses which confirm that these quick clays were originally sedimented in almost fresh water, salinity about 3 per thousand.

When investigating the present salt content of the pore water in the Ancyclus clay, Keinonen found the salinity to be on average 1,2 per thousand, i.e. only slightly

lower than that during the time of sedimentation. This confirms the fact that practically no leaching had occurred. Keinonen has, however, not investigated the ionic composition of the pore water.

Penner (1965), Talme et al. (1966), Talme (1968) and Söderblom (1969) have found that normal clays ( $S_t = 10 \text{ \AA } 20$ ) and quick clays with approximately the same total salt content can occur within a short distance in the same sedimentation area. This has been found in the case of both marine and non-marine clays. The quick clays differ, however, from the normal clays in pore water composition. Quick clays have pore water with sodium as the dominating cation, while normal clays have calcium and magnesium as dominating cations. Söderblom (1969) has shown that this difference cannot be explained by means of simple diffusion or leaching processes. By means of leaching, experiments he has shown that the Donnan conditions are valid in a clay system (cf. Ch. 2.3.1 in this report). A leaching of a salt clay containing the ions  $\text{Na}^+$ ,  $\text{K}^+$ ;  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  will cause a relative enrichment of the divalent cations and thus lead to a normal clay. Söderblom also showed that the apparent deviation from the Donnan conditions displayed by the quick clays is caused by complex binding or precipitation of the divalent ions and not by their removal from the clays. By suitable treatment these

ions could be set free.

### 3.2 Ground Water Composition and Leaching

In the classical leaching theory some general statements are made, viz.,

- 1) the clays are precipitated in sea water having a high content of sodium ions,
- 2) the clays are leached in such a manner that a system with a low total salt content and an ion composition with  $\text{Na}^+$  as dominating cation is obtained.

The leaching in situ is due to ground water movement. Therefore the composition of the ground water is a very important factor in the discussion of the effect of a natural leaching.

In Sweden, two main types of ground water occur. The first type is the so called hard water having  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as dominating cations. If a clay system independent of its ionic composition is affected by such a ground water, a system having divalent ions as dominating cations occur (cf. Ch. 2.3.1). It is thus clear that in areas with a hard water, no naturally formed high sensitive clays with  $\text{Na}^+$  as dominating cations can occur.

The second type is soft ground water having  $\text{Na}^+$  as dominating cations. It is evident that one main condition for transforming a normal clay with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as dominating cations is that the "leaching" water has a sufficient amount of  $\text{Na}^+$  and a lack of  $\text{Ca}^{2+}$   $\text{Mg}^{2+}$  (soft water).

Ground water in nature, seepage problem, the location of ground water and its importance for the formation of quick clays with different rapidity numbers have been treated to some extent in an earlier report by Söderblom (1974).

It should also be mentioned that a precipitation of the clays in sea water is no necessary condition for the transformation of normal clays into high sensitive clays (quick clays). If a normal clay is influenced for

some time by a water rich in  $\text{Na}^+$  and containing "water softeners" (detergents), etc., a clay system with a pore water corresponding to that of a quick clay will be formed. Waters of this kind are relatively common in populated areas with leaking sewage systems.

### 3.3 The Problem of Rapidity in the Quick Clay Research

If the rapidity number is taken into consideration, new aspects must be formed regarding the formation of quick clays. Quick clays with high rapidity number, i.e. clays being liquified by a very small working, seem so far to be rare in Sweden. They can be found in areas rich in ground water seepage streaks. But as has been shown by Söderblom (1974), there is no direct connection between such streaks and high rapid quick clays. In streaks with hard ground water (cf. Ch. 3.2) such clay is not formed.

The great difference in strength properties between quick clays of the high rapid type and the low rapid type indicates that these two types have different cementing and dispersing conditions. The classical leaching theory takes, of course, no consideration to the new concept rapidity and according to the theory, given by e.g. Lambe, of the instable cardhouse structure, it can be concluded that only clays with a very high rapidity number will suit this theory.

The leaching theory has been ascribed as the original Norwegian quick clay forming theory. It is, however, remarkable to find that the old Norwegian geologists had observed that quick clay slides occurred in connection with peat mosses. This was, e.g., the case at Vaerdalen (cf. Tesaker, 1958; Brögger & Münster, 1893). Brögger (1893/94) proposed to the Norwegian Ministry of Public Work that all peat mosses in the vicinity of clay slopes should be ditched out.

The quick clay forming process must be regarded as a complicated colloid chemical reaction process as stated by Rosenqvist (1966). One of the most important factors in this process is shown to be the influence of dispersing agents of either inorganic or of organic origin.

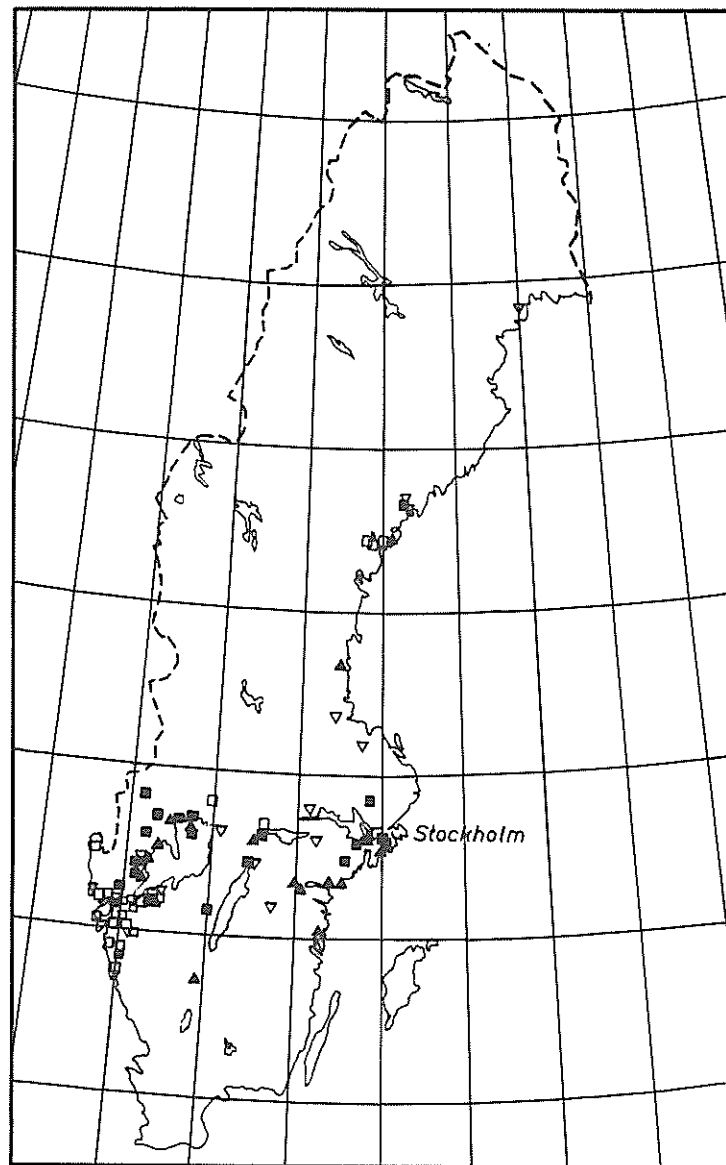


Fig. 1 Map showing the occurrence of different types of quick clays in Sweden

- ▽ non-varved quick clays in connection with peat or other organic materials
- ▲ varved quick clays in connection with peat or other organic materials
- other non-varved quick clays
- other varved quick clays

### 3.4 Archive Studies

In order to investigate whether varved quick clays are common or not in Sweden an archive study was performed at the Swedish Geotechnical Institute (SGI). (A comprehensive geotechnical archive is also available at the Swedish State Railways.) Another purpose was to get indication on places where quick clays with high rapidity number could be found.

A number of 1448 consecutive reports from SGI carried out in the years 1960-1965 were studied. The location of the sites is given in the map in Fig. 1. Quick clays in the meaning of high sensitive clays occurred in 62 cases, i.e. 4.3% of all. Of them, 26 cases were varved fresh-water deposited quick clays and 36 cases probably marine clays.

In one case quick clay was found above the highest marine shore line (Hillerstorp in Småland) and this deposit cannot possibly have anything to do with sea water.

The other 61 deposits are situated below the highest marine shore line. From the type of clays, rough conclusions can be drawn of the sedimentation environment (no results from diatom analyses are found in the archives). Thus, varved fresh-water deposited quick clay is hardly less common than marine clays. Most of the quick clay deposits are relatively local. No large areas containing quick clays have thus been found. It was observed that the sensitivity as a rule shows very large variations according to depth.

The archives contain no direct information on the rapidity properties of the quick clays. Since the high rapid quick clays have properties which makes it possible to distinguish them, they could sometimes be detected indirectly in the archives. Such clays show as a rule syneresis, in the archive record indicated as "free water". Very often these samples are found to be severely damaged by sampling and transportation. These are marked "sample disturbed" in the records. Sometimes such samples also seem to show remarkably low shear strength measured with the unconfined compression test and compared with the cone test.

The archive studies so far made give a tentative review of quick clays distribution in Sweden and their sedimentation environment. They should be completed and result in a map with the geographical distribution of different types of quick clay.

It must be stressed that this archive material is derived from transported and stored samples. As seen in, e.g. Söderblom (1969), ageing effects may have changed the sensitivity both to smaller and higher values. It may be added that the samples also have been taken with different samplers giving different disturbances.

It is also possible to draw, indirectly, the conclusion from the archive study that quick clays with very different properties, e.g. different rapidity, exist in Sweden. The quick clay deposits are local and surrounded by normal clays. Quick clays and normal clays are thus found in the same sedimentation area. This seems to exclude such processes as salt leaching by diffusion at the formation of quick clay.

Earlier a similar archive study was made by the Geotechnical Department of the Swedish State Railways by Jerbo & Hall (1961). The results of their studies are summarized in the map reproduced in Fig. 2. As seen on the map, in some cases quick clay was found in the immediate vicinity of organic layers. This was especially the case of the sulphide-banded clays located in northern Sweden.



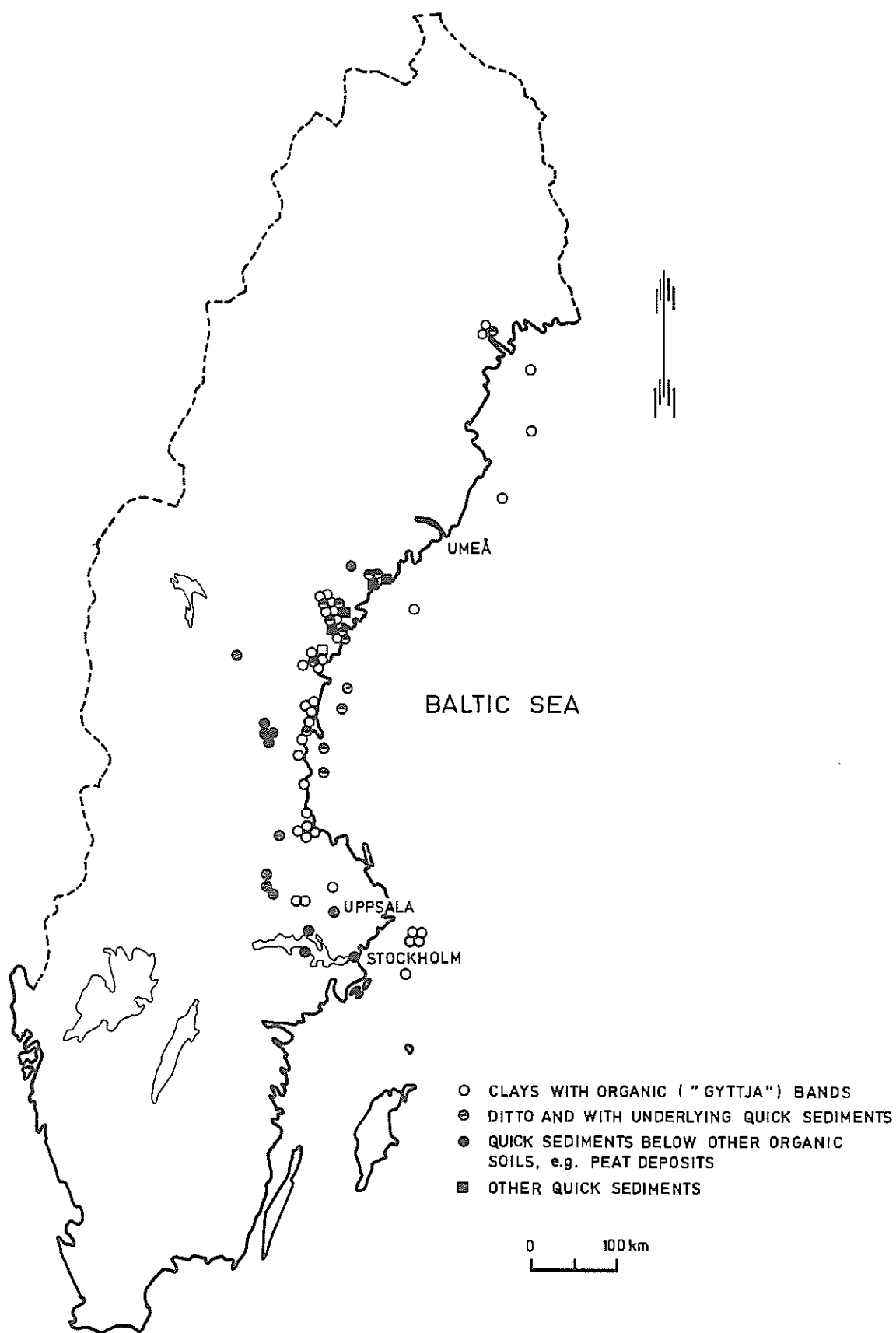


Fig. 2 Map showing occurrence of different types of quick clays in eastern Sweden (after Jerbo & Hall, 1961)

## 4. PRESTUDIES ON THE IMPORTANCE OF ORGANIC MATERIAL TO SOME QUICK CLAY PROPERTIES

### 4.1 Ionic Composition of the Pore Water and Adsorbed Double Layer

As mentioned in the Introduction and as seen from Söderblom (1969) quick clays have an ionic composition in their pore water with sodium as the dominating cation. According to Ch. 7.4.1 a leaching of a system consisting of clay minerals, water and ions would lead to a clay with a pore water having mainly divalent ions, thus according to all definitions a non-quick clay. The first question is therefore if organic material can act in such a way that the ionic composition of the pore water of a clay is changed to that of a quick clay. A series of experiments was therefore made. One typical experiment to obtain an answer to the question is the following.

Hymatomelanic acid (about 1 g in 100 g clay) was added to kaolin 46 (cf. Söderblom, 1969) with  $H_1 \approx 10$  until minimum strength value of the suspension was obtained ( $H_1 < 0.33$ ). Pore water was squeezed out and a small chromatogram shown in Fig. 3 indicated that the change discussed above in pore water composition did occur.

Kaolin 46 containing hymatomelanic acid (2 g per 1000 g) was sedimented in synthetic sea water. The sediment was decanted and dialysed to  $R \approx 400$  ohm. The pore water was thereafter squeezed out from the dialysed kaolin and examined chromatographically, Fig. 4. Also in this case the pore water composition was changed.

From these experiments it is seen that organic substances existing in nature have the properties of being able to change the ionic composition of the pore water of a non-quick clay to that of a quick clay. The ionic composition of the double layer of a quick clay and a leached non-quick clay was studied in a series of experiments. The clays of the two types originated from some places in the Göta River Valley (Utby, Älvängen etc.).

The procedure was as follows. 2 g of clay was sus-

pended in 100 ml of 1N  $\text{NH}_4\text{Ac}$  solution and the mixture was allowed to react for 6 hours. Thereafter the suspension was centrifuged and the solution obtained was evaporated and studied with paper chromatography. The results are shown in Figs. 5a and 5b. The main ions in the double layer were calcium, magnesium and sodium. No principal distinction between quick and non-quick clays could be found. Both quick clays and non-quick clays are rich in divalent ions in the double layer.

The results are in accordance with investigations on the double layer composition of quick clays from Drammen, Norway, reported by Moum, Løken & Torrance (1971). In their investigation it is shown that quick clays and leached non-quick clays differ in pore water composition but no similar distinction can be found in the double layer (cf. Table 1 in their paper). It is also confirmed that both quick and non-quick clays are rich in divalent ions in the double layer.

### 4.2 Studies of the Macro-Structure of Quick Clays

#### 4.2.1 General

As seen in Ch. 1, Swedish quick clays, irrespective of their rapidity number, show the same pattern of weak zones as described by Eden & Mitchell (1970) for Leda clay (this also applies to certain normal Swedish clays). The feature is illustrated in Fig. 6 showing a piece of quick clay from Ellbo, taken at a depth of 15 m, initially broken into two pieces and then further broken into small pieces or nodules.

Experiments in the laboratory to make synthetic quick clays have so far taken no consideration to the above-mentioned structural characteristics. Sedimentation-consolidation experiments give a homogeneous structure as shown in Ch. 4.2.2. With humus precipitation in a clay gel it is, however, possible to obtain such a nodule structure.

The cardhouse-structure theory states a homogeneous

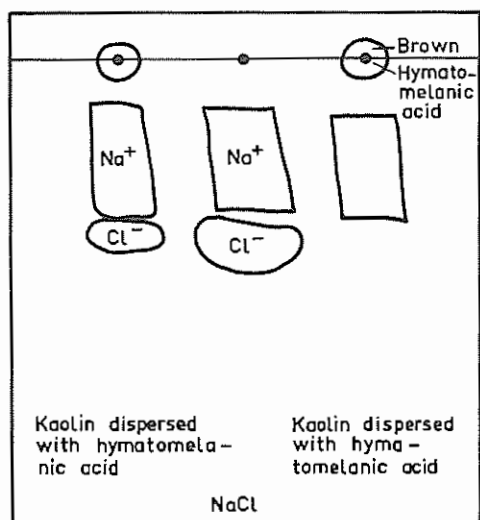


Fig. 3 Small-paper chromatogram of "pore water" of a paste of "kaolin 46" dispersed to minimum viscosity by hymatomelanic acid

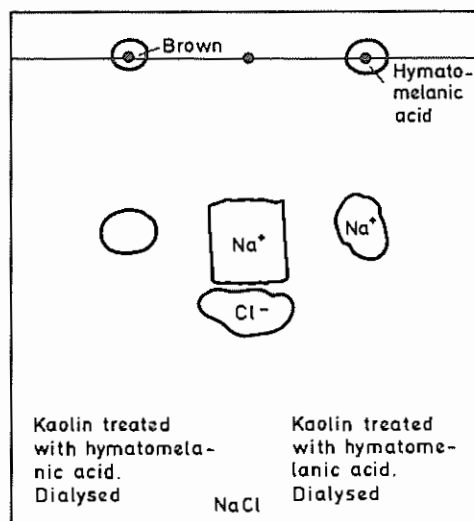


Fig. 4 Small-paper chromatogram of "pore water" of a paste of "kaolin 46" dispersed to minimum viscosity by hymatomelanic acid coagulated with NaCl and leached with distilled water

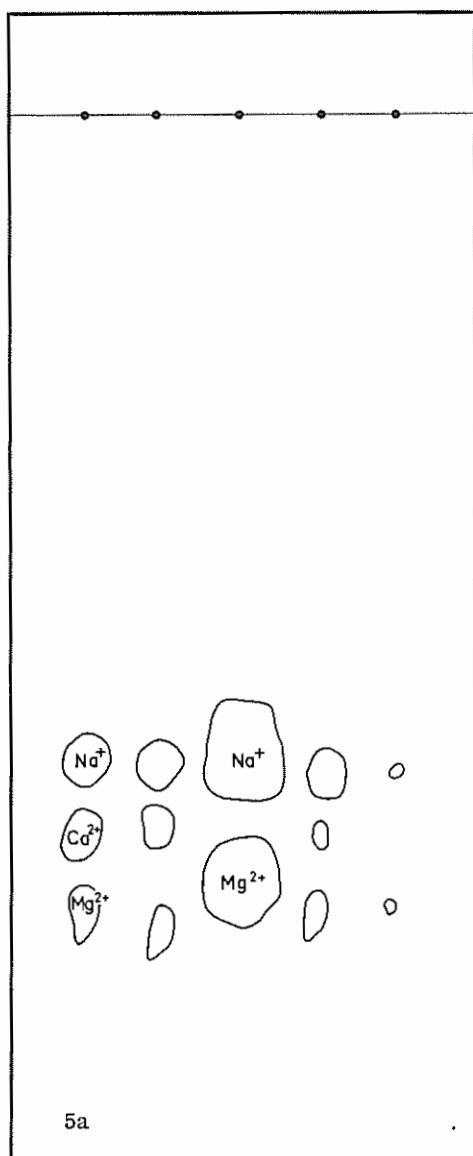
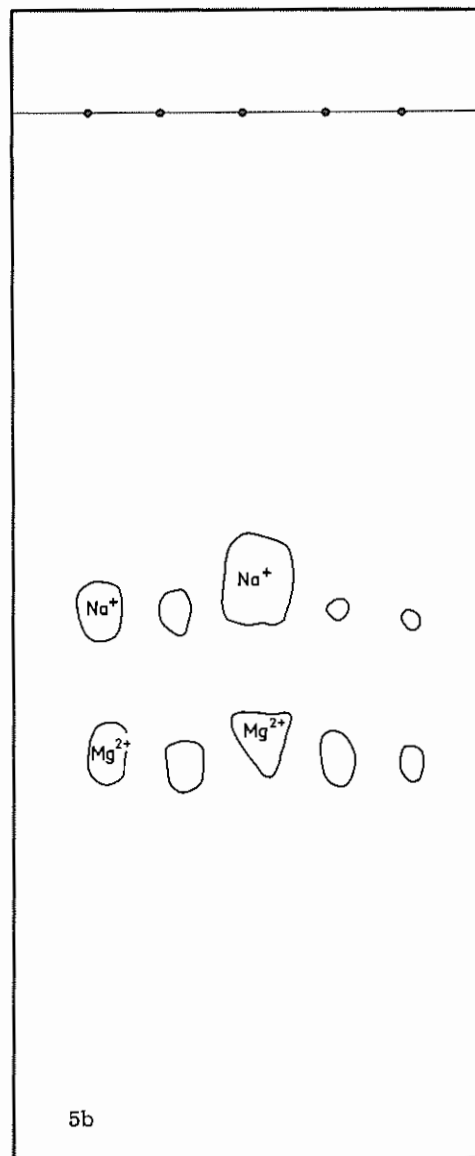


Fig. 5a-b Paper chromatogram of the  $\text{NH}_4\text{Ac}$  eluate from a clay from Utby Hole 658, 12 m and a clay from Utby Hole 99, 9 m



structure without fissures of any kind.

#### 4.2.2 Experiments on Artificial Quick Clays

Several attempts to make artificial quick clays have been reported in a literature, e.g. Bjerrum & Rosenqvist, (1956), Pusch & Arnold, (1969), Pusch (1973). In some cases the authors have succeeded in building up a sensitivity of more than 50. No considerations have, however, been taken to the structure mentioned above.

In the present investigation hydrogenperoxide-treated quick clay material from Utby, Hole 658, was sedimented in synthetic sea water (according to Sverdrup et al., 1942). The excess of sea water was decanted and the sample obtained was consolidated in a filter-press with a pressure of  $2 \text{ kg/cm}^2$ . Thereafter the sample was mounted in a dialysis membrane and dialysed to  $\kappa \approx 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Attempts were made to break the sample into pieces as was done with the natural quick clay in Fig. 6 but it proved impossible. No fissured structure was obtained in this experiment as shown in Fig. 7 (kaolin) and it seems that experiments of this kind cannot be used as a model for the process in nature.

A clay gel containing organic matter was also prepared. 100 g kaolin ( $H_1 \approx 10$ ) (cf. Söderblom, 1969) with a pore water containing 4 g glyccoll and 1 g glucose was kept in  $90^\circ\text{C}$  water for 10 hours. A kaolin containing synthetic humus (melanoidin) was obtained. It was found that a fissured pattern was formed and that the melanoidin precipitated into the fissures. It was possible to break this kaolin material into pieces as in the case of the natural Utby quick clay. Fig. 8 shows a picture of such a kaolin piece.

It is thus possible to obtain a clay sample with a structure similar to that existing in nature by means of precipitation of synthetic humus.

### 4.3 Supplementary Studies

#### 4.3.1 Influence of Hydrogen Peroxide on Chemical Properties of Quick Clays

As stated in Ch. 2 in this report, organic material is complex-binding calcium and magnesium ions in the quick clays. A hydrogen peroxide treatment which will partly destroy the organic material of such a clay will therefore lead to the liberation of these ions causing an accumulation of them in the pore water. This is illustrated in Fig. 9. After treatment with hydrogen peroxide (cf. below) a quick clay with sodium as the dominating cation has got a composition with calcium and magnesium as dominating ions. Also iron(III) ions are present in the pore water. This is easily detected by spraying the chromatogram with potassium rhodanide. Such a peroxide-treated quick clay system shows no stiffening effect if sodium chloride is added, as shown in Fig. 10.

The hydrogen-peroxide treatment was made as follows. 500 g of natural moist clay was suspended in about 1 litre of 15% hydrogen peroxide and was allowed to react for 24 hours. The temperature rose to about  $50$  to  $60^\circ\text{C}$  during the reaction and then dropped. No outer heating was present. Thereafter, about 500 ml of 15% hydrogen peroxide was added and the mixture was allowed to stand for a further period of 24 hours.

#### 4.3.2 Colloid Chemical Differences between Slow and High Rapid Quick Clays

As shown by Söderblom (1974) high rapid and slow quick clays have very different remoulding properties. Samples of the first type are in extreme cases practically impossible to handle while samples of the second type are relatively insensible to moderate working.

As seen later in this report, all quick clays contain dispersing agents. Table 1 shows the results from a series of dialysing experiments on different clays with varying dispersing agents. It is obvious that the rapidity number changes due to the treatment. Especially dispersing agents containing phosphate increase the rapidity number of the clays.

Clays of the rapid and the slow type may differ with respect to the content of cementing gels. According to Pusch (1973) both iron hydroxide gels and organic gels act as cementing agents. McGauhey & Krone (1967) have found that sewage attacks iron gels and

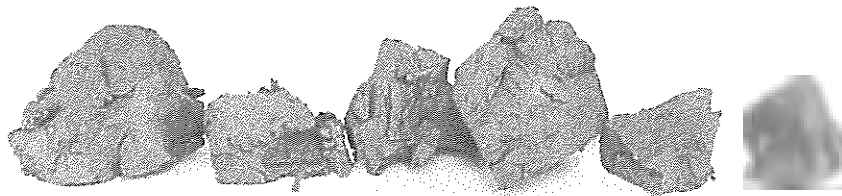


Fig. 6 Quick clay sample broken into pieces indicating a nodular structure

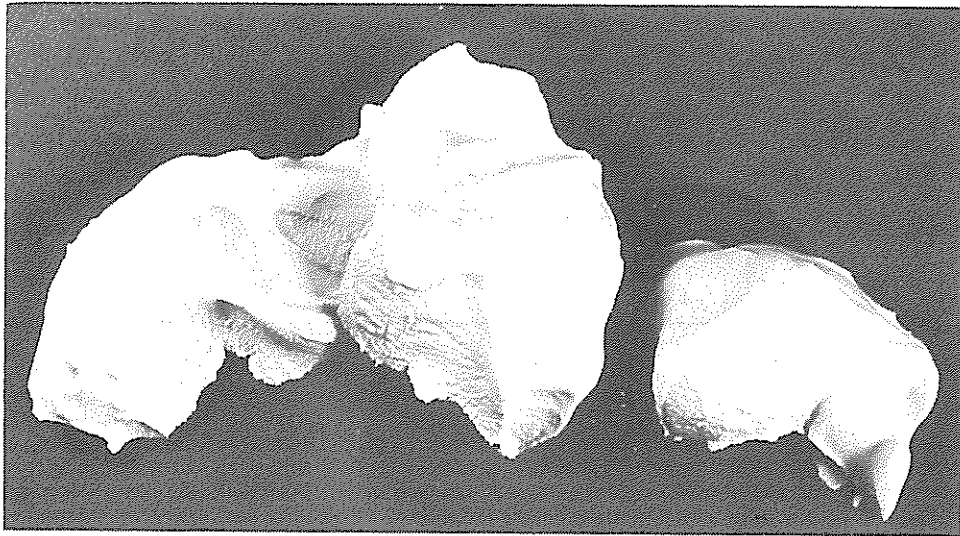


Fig. 7 Homogeneous structure of a synthetic "quick clay" (of kaolin)

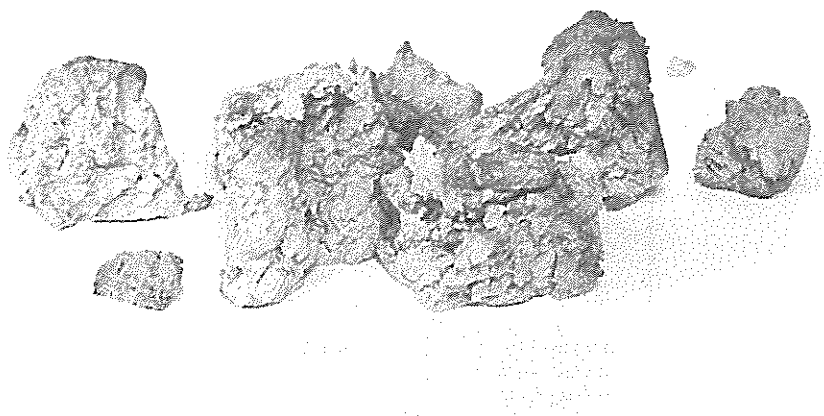


Fig. 8 Nodular structure of a synthetic "quick clay" produced by humus precipitation in kaolin

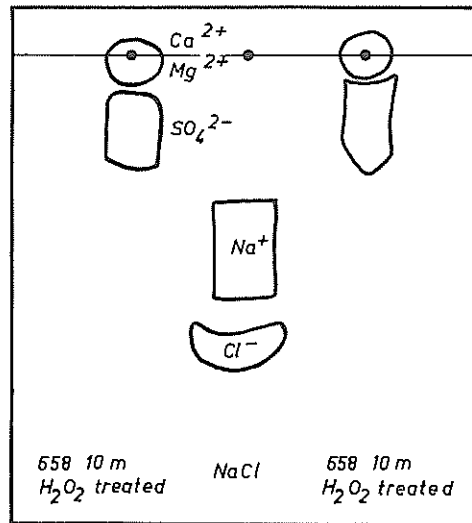


Fig. 9 Small-paper chromatogram of pore water of a clay from Utby, Hole 658, 10 m, treated with  $H_2O_2$

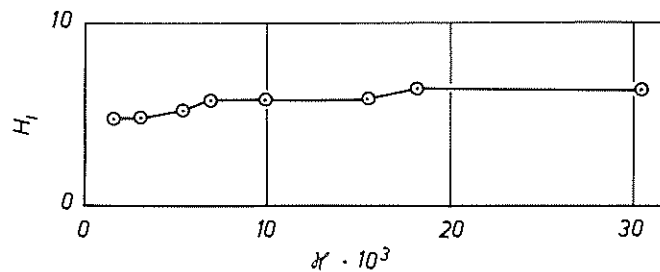


Fig. 10 Relation between conductivity (salt content) and  $H_1$ -value for a quick clay from Utby, Hole 658, 15 m, in which the organic material has been destroyed with hydrogen peroxide ( $\kappa$  given in  $ohm^{-1}cm^{-1}$ )

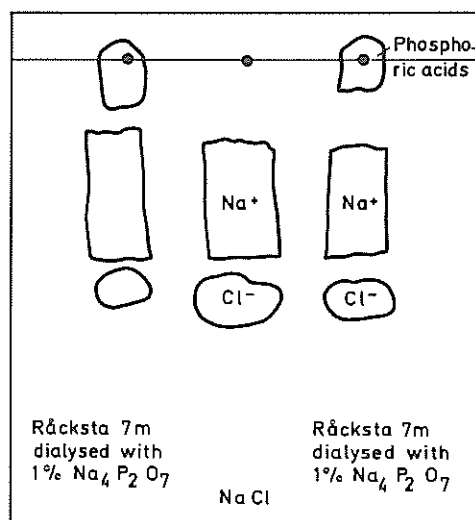


Fig. 11 Small-paper chromatogram of pore water salts in clay sample dialysed with 1% sodium pyrophosphate



Table 1 Results from dialysis experiments

Sample from Depth	Hole	Treatment	H <sub>3</sub>	H <sub>1</sub>	H <sub>3</sub> /H <sub>1</sub>	w %	w <sub>L</sub> %	R <sub>n</sub>	pH	R
L. Edet 14 m	4845	-	168	1.45	116	69	54	3		
		24 hrs dial. dist H <sub>2</sub> O	63	0.33	189	80	48	9		
		24 hrs dial. sewage	66.2	0.384	174	77	48	7		
		24 hrs dial. sewage conc.	95.5	0.522	183	75	43	6		
5 m	4956	-	145	1.84	79	81	-	4		
		24 hrs dial. with dist. water	101	0.33	306	86	43	8		
		24 hrs dial. sewage	120	0.562	212	-	65	8		
Jordbro 7 m	2084	-	20.4	6.93	3.0	31	26	7		
		24 hrs dial. sewage	20.4	4.9	4.2	31	28	8		
		24 hrs dial. toilet soap	1.66	0.454	3.6	31	50	9		
	3851	-	28.8	4.9	5.9	31	26	7		
		24 hrs dial. 1% Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	23	0.33	70	30	16	8		
		24 hrs dial. dist. water	37.6	4.9	7.7	34	31	7		
		24 hrs dial. 1% wash. ag.	8.2	0.5	16.4	-	28	9		
8 m	VFS484	-	47.9	1.09	43.9	47	33	6	7.6	820
		24 hrs dial. sewage conc.	44.1	2.58	17.1	47	-	7	8.6	650
		24 hrs dial. 1% wash. ag.	17.0	0.33	51.5	49	29	9		
9 m	3006	-	24.2	4.6	5.3	26	22	7		
		24 hrs dial. 1% wash. ag.	17.0	0.38	45	22	20	10		
		24 hrs dial. 1% Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	28.2	0.33	85	56	-	9		
Räcksta 2 m	306	-	15.8	4.09	3.86	60	51	7	8.2	270
		24 hrs dial. sewage conc.	12.6	2.72	4.64	60	48	8	8.6	320
	649	-	25.0	2.58	9.7	67	45	5		
		24 hrs dial. 1% ferro chr. lign.	10.5	0.33	32	61	35	8		
	1086	-	42.4	5.4	7.5	62	54	6		
		24 hrs dial. sewage	34.2	3.8	9.0	-	-	6		
		24 hrs dial. toilet soap	23.2	1.66	14	-	23	6		
3 m	119	-	63.0	4.9	12.9	52	51	7		
		24 hrs dial. wash. ag.	34.8	3.6	9.7	-	52	7		
		24 hrs dial. dist. water	52.2	4.93	10.6	-	53	7		
4 m	295	-	37.6	4.44	2.5	63	51	4		
		24 hrs dial. Lignosite	30.0	2.9	10.3	60	50	5		
	718	-	33.0	2.29	14.4	75	55	4		
		24 hrs dial. 1% melanoidin	22.3	1.37	16.3	95	63	5		
5 m	775	-	34.2	1.84	18.6	72	48	5		
		24 hrs dial. 1% hymath. ac.	17.9	0.60	29.8	77	56	9		
7 m	38	-	27.1	4.44	6.1	61	50	5		
		24 hrs dial. Lignite	21.1	0.445	48	77	50	8		
	529	-	44.1	1.15	21.4	55	47	4		
		24 hrs dial. 1% sodium ox.	30.0	0.60	50	69	34	7		
	663	-	40.0	2.50	15.5	66	49	5		
		24 hrs dial. 1% Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	33.0	0.33	100	68	27	8		
8 m	368	-	49.0	2.58	19	61	48	4		
		24 hrs dial. 1% water-gl.	42.4	0.33	120	55	52	2		

leaches out iron ions. It is, however, difficult to show the amount of cementing gels directly by colloid chemical investigations. One possible, indirect method is to use the decrease of the liquid limit by pre-drying and re-vetting. According to Casagrande (1939) this decrease is a measure of the effect of the cementing organic gels.

#### 4.4 Discussion and Conclusion

The experiments with the composition of the adsorbed double layer indicated that there is hardly any relation between the double layer composition and the sensitivity of a clay. It shall be noted that the double layer is rich in divalent ions both in quick clays and in non-quick clays. The double layer of the quick clays, rich in calcium-magnesium, is in equilibrium with a pore water with sodium as the dominating cation, and indicates the presence of substances decreasing the calcium-magnesium activity in the pore water (dispersing agents).

The sedimentation-consolidation experiments showed that it is impossible to build up artificially quick clay with the nodule structure occurring in nature and that the cardhouse structural theory is not per-

tinent in this respect. It is, however, possible to build up such a nodule structure by means of precipitation of humus gels in the clay colloid.

The formation of a structure with micro-fissures by precipitation of a gel in another gel is a relatively unknown phenomenon in colloid chemistry and as far as the present Author is aware no consideration has yet been taken to such a process in the quick clay formation. This is, however, of the greatest importance to the understanding of the chemical processes in connection with ground water flow in quick clays. The problem is also reflected in the absence of short-term ageing processes in situ. It is also included in the slope stability problem. If a fissured structure combined with syneresis occurs, it is possible for the water to find its way into the fissures giving rise to local seepage. The problem should be treated further, at best in combination with chemical stabilization experiments.

The experiments with hydrogen-peroxide treatment of quick clays showed that such clays are very rich in masked divalent cations. This indicates that clay strength properties can be easily changed which is in practice shown by experience of quick clay stabilization experiments (cf. Talme, 1968 and Jerbo, 1972).

### 5. ORGANIC MATERIAL AND ITS IMPORTANCE TO CLAY PROPERTIES

#### 5.1 General

Organic material has at least three different modes of action on clay. Firstly, it can act as cementing gels, giving the soil an aggregated structure. Secondly, the reaction during hypergenesis gives rise to a fissured structure of the clay accompanied by syneresis. Thirdly, it can act as dispersing agents.

##### 5.1.1 Cementing Organic Substances

According to Kononova (1961) organic material is very

important to the formation of the structure of the soil. She cites several authors treating this problem, for example Savvinov (1935), Gupta & Sen (1962) state that an aggregated (cemented) structure is formed if soil material is treated with, e.g., glucose and allowed to stand under special bacterial conditions. Soil-forming aggregates are built up by microbial activity. Several authors (e.g. Flaig & Beutelspacher, 1954) have found that organic linear colloids contribute to the cementation of clays and have shown by means of electron micrographs that "threads" have been formed giving a network binding the clay particles together more strongly. Further information of works treating this

important role of the organic material has been given by Scheffer & Ulrich (1960). Pusch (1973) states that organic material can have a cementing effect in quick clays and influence their strength properties. By remoulding an organic clay, the organic cementing bindings are broken and the clay will lose parts of its shear strength. It should also be added that silicon organic bindings in clays can occur.

The chemical fabric of the cementing organic colloids is rather unknown. They are possibly condensation products of amino acids with polyphenols, sugar and other substances.

This question is, however, outside the scope of this work.

### 5.1.2 Dispersing Organic Substances

A group of organic substances which is very important to the understanding of the quick clay chemistry is, as said before, the dispersing agents. This group contains substances which can be analysed and will be studied further.

Bloomfield (1954 and 1956) has found that kaolin can be deflocculated by different natural leaf extracts. He asserts that in some cases polyphenols are the cause of the observed dispersing effects but gives no definite proof. Hence, polyphenols are one group of compounds whose clay dispersing properties must be examined and their possible presence in quick clays be checked.

With the exception of these few references, the literature does not seem to give any direct hints as to the nature of substances being able to cause quick clay formation in nature. For studies of clay deflocculation in general, on the other hand, a great amount of literature is available. Especially works on drilling mud is of interest.

A summary of the most common dispersing agents used in the drilling mud industry is shown in Table 2 (cf. Rogers, 1963). As seen from this table, active dispersing agents are of both inorganic and organic nature. The organic agents in particular belong to

very different groups of substances. As noted there is a great variety of substances which must be tested with regard to their dispersing properties and their possible appearance in quick clay.

In the table some substances of inorganic nature are also given. Their importance to the quick clay formation will be treated below together with the organic substances.

The dispersing substances are in detail treated in Ch. 5.2.

### 5.1.3 Organic Materials with Other Properties

In nature there are organic materials with the ability of breaking down the structure of minerals. This is the simplest form of activity of organic substances on such mineral parts as phosphates and carbonates, etc. Many acids formed by microbial action have this effect (cf. Ravich-Shcherbo, 1928). This type of activity is further discussed in connection with the importance of peat to the quick clay formation.

Gases are often present in quick clays due to anaerobical decomposition of different organic products (Jerbo, 1967). Sometimes these gases can have coagulating properties giving rise to changes in the sensitivity when the samples are intensively remoulded.

## 5.2 Dispersing Agents

### 5.2.1 Inorganic Dispersing Agents

The inorganic dispersing agents given in Table 2 are silicates and phosphates.

The best known of the simple silicates having dispersing properties is water glass. Chemically it is a silicate solution of rather undefined composition. From water glass it is easy to produce a well defined silicate  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  (Vesterberg, 1914). Also this salt has some dispersing properties as shown in Ch. 6.

Lagerström (1959) has studied the equilibrium between

Table 2 Compounds proposed for reducing of the viscosity of drilling muds (from Rogers, 1963)

<p>A. Commercial Alkalies</p> <ol style="list-style-type: none"> <li>1. Sodium silicate</li> <li>2. Monosodium phosphate</li> <li>3. Disodium phosphate</li> <li>4. Trisodium phosphate</li> </ol> <p>B. Molecularly Dehydrated and Polyphosphates</p> <ol style="list-style-type: none"> <li>1. Sodium pyrophosphate</li> <li>2. Sodium acid pyrophosphate</li> <li>3. Sodium metaphosphate</li> <li>4. Sodium tetraphosphate</li> <li>5. Sodium tripolyphosphate</li> <li>6. Sodium heptaphosphate</li> <li>7. Sodium octophosphate</li> <li>8. Esters of pyrogallol and orthophosphoric acid</li> <li>9. Esters of sodium gallate and metaphosphoric acid</li> <li>10. Salts of hexaphosphate dinitride</li> <li>11. Alkali metal hexametaphosphate fused with oxygen-containing boron compounds</li> <li>12. Alkali metal pyrophosphates plus borax or boric acid</li> <li>13. Amino-phosphates</li> <li>14. Alkali metal thiotetraphosphates</li> <li>15. Alkali metal phosphates plus polybasic aliphatic acids</li> <li>16. Complex alkali metal heavy metal polyphosphates</li> </ol>	<p>D. Lignosulfonates</p> <ol style="list-style-type: none"> <li>1. Calcium lignosulfonate</li> <li>2. Sodium lignosulfonate</li> <li>3. Aluminum lignosulfonate</li> <li>4. Ferro chrome lignosulfonate</li> <li>5. Ammonium chrome lignosulfonate</li> <li>6. Oxidized waste sulfite liquor</li> </ol> <p>E. Mined Lignins (Humates)</p> <ol style="list-style-type: none"> <li>1. Humic acid plus sodium hydroxide</li> <li>2. Mined lignins</li> <li>3. Mixtures of mine lignins and tannins</li> <li>4. Methylenic sulfonated alkaline lignin</li> <li>5. Water soluble lignite sulfonates</li> </ol> <p>F. Others</p> <ol style="list-style-type: none"> <li>1. Urea</li> <li>2. Thiourea</li> <li>3. Polyphosphoric acid with urea</li> <li>4. Dicyandiamide</li> <li>5. Polyphosphoric acid compounds with dicyandiamide</li> <li>6. Substituted ureas</li> <li>7. Substituted thioureas</li> <li>8. Carboxylic acid amides</li> <li>9. Alkaline quinone and quinhydrone</li> <li>10. Water soluble derivatives of metal oxides or Periodic Table groups III, IV, V, VI</li> <li>11. Pectin plus sodium hydroxide</li> <li>12. Pentosans and hexoses</li> <li>13. Pentosans and hexoses plus polyphosphates</li> <li>14. Pyrovic acid and alkaline salts of the same</li> <li>15. Alkali metal alkyl silicate</li> <li>16. Alkaline coal extract</li> <li>17. Sodium salt of Ethylene Diamine tetraacetic acid</li> <li>18. Hydrolyzed polymers of hydrocyanic acid</li> <li>19. Oxidized petroleum acid</li> </ol>
<p>C. Tannin Compounds</p> <ol style="list-style-type: none"> <li>1. Condensation products of organic hydroxy groups as sugar, starch, tannins with acidic oxides of phosphorus, vanadium and arsenic</li> <li>2. Pecan hull lining</li> <li>3. Quebracho extract</li> <li>4. Chestnut extract</li> <li>5. Divi-Divi extract</li> <li>6. Wattle bush extract</li> <li>7. Mangrove extract</li> <li>8. Hemlock extract</li> <li>9. Redwood extract</li> <li>10. Gallic acid</li> <li>11. Quebracho extract plus sodium stannate</li> <li>12. Redwood bark-caustic reaction mixture</li> <li>13. Calcium oxide, soda ash, quebracho mixture</li> <li>14. Heavy metal ion, phosphate, tannin, or humic acid mixture</li> <li>15. Tara pods</li> <li>16. The above reacted with caustic and dried</li> <li>17. Quebracho and sodium meta-aluminate</li> </ol>	

different soluble silicate ions (in a perchlorate solution). He did not, however, find any method of making direct measurements on the anions but had to make his calculations on the basis of the hydrogen and hydroxyl ions in the solution.

The Author knows of no analytical method permitting the separation and identification of soluble ions of different forms. Great difficulties will appear if one tries to isolate silicates from a quick clay by chemical means. As stated earlier (Söderblom, 1969) the clays are easily affected by chemical weathering if treated with e.g. salt solution, resulting in an increased salt content. Such processes also liberate silicate ions.

Kvyatkovskaya & Chernov (1960) have suggested that all clay dispersing reactions are due to the formation of silicates. According to these authors' oxalates and other well known dispersing agents should react with the clay minerals, forming silicates which give a dispersing effect. Michaels (1958) states that silicic acid will appear when kaolin is dispersed by polyphosphates and he maintains that silicic acid is a reaction product in the dispersing process. Michaels has, however, not shown the existence of silicic acid chemically. From the electron-neutrality relation he has concluded that an unknown ion X must exist, which he considers to be a silicate ion. Ions of silicic acid are therefore expected as one of the quick clay components.

As said above organic materials exist being able to break down the structure of minerals. The remaining part consists of amorphous silicic acid. A clay treated by, e.g., acids from peat, lichens, etc., would contain an excess of silicate ions adsorbed to the clay particles, binding calcium and magnesium ions suppressing the expected Donnan effect. A suppressing of this kind is, as known, necessary for the formation of a quick clay.

According to Miller (1968) acids give an edge attack on kaolinite particles and this reaction results in the formation of amorphous silicates. The formation of quick clay in connection with peat may be caused by such a process, but the strong dispersing effect of the residue obtained by evaporation of peat water indicates also that dispersing processes are included.

One can also expect soluble silicates present in the synthetic detergents to be of importance to the formation of quick clays. Substances of this kind have in recent years gained an increased use in households, etc. Under unfavourable conditions they can be infiltrated in the ground from discharge conduits. Several authors, e.g. McGauhey & Krone (1967) and Sepp (1973) have observed that waste water infiltration causes a dispersing attack of clay minerals especially under anaerobic conditions.

The second inorganic dispersing agent is sodium salts of different phosphoric acids. Phosphates are found by the Author to be of very great importance in the formation of quick clays with high rapidity number. In all cases found hitherto these phosphoric acids originate from domestic sewage (cf. Söderblom, 1973).

Phosphoric acids, possibly organic, are common plant components. According to Nykvist (1963), these acids show a rather great resistance to consumption by microorganisms. It is possible that some part of the phosphoric acids present in quick clays can originate from plant residues.

### 5.2.2 Organic Dispersing Agents

According to Kononova (1961) the organic soil constituents can be divided into two groups, viz., "substances of individual nature" and "substances of strictly humic character". Generally, it can be said that a great number of substances belonging to the first group have been isolated and identified. Attempts to determine the structure of the real humus substances have hitherto (1974) not been very successful owing to their complexity, instability and variety in chemical composition.

Organic dispersing agents can be found in both groups. The substances of individual nature occur, however, in natural, unaffected soil material in relatively small amounts. Quite other conditions are, of course, prevalent in urban areas. The experience obtained indicates the necessity of studying both groups.

### 5.2.3 Organic Dispersing Substances of an Individual Nature

#### 5.2.3.1 Substances of Carbohydrate Nature and Hydrocarbons

Carbohydrates are of interest both in free form and as part of more complex dispersing agents. Emerson (1954) and Bloomfield (1956) assume polysaccharides to be active dispersing agents in nature.

As stated in Ch. 4.3.1 carbohydrates and amino acids can react and form brown substances, melanoidin, with strong dispersing properties. Substances of this kind are easily hydrolysed by acids and the carbohydrates can be analysed.

Nykvist (1963) has found simple sugars in leaf extracts, but they were rapidly destroyed by micro-organisms. Sörensen (1967) has studied the behaviour of carbohydrates added to soils. He found that  $^{14}\text{C}$ -glucose was transformed into amino acids by microbial action.

Carbohydrates are very suitable substances for the growth of microorganisms and therefore the presence of carbohydrates in the ground can give support to a microbiological activity yielding products which are strong dispersing agents. Uronic acids may be such components.

The saponines are of great interest in this connection. Chemically they belong to the category of tripen-glucosides and steroidglucosides. Saponines are very often effective dispersants and are products formed by microbial processes. The Author expects that they are to be found in peat water and in quick clays. Forsyth (1947) has found similar products, phenolic glucosides, in the fulvic-acid fraction of soil organic matter, and Kwiatkowski (1965) has found terpenes in the unsaponifiable part of peat bitumen.

Hydrocarbons are very common in clay and peat. At present it seems difficult to distinguish between hydrocarbons formed by natural processes and hydrocarbons infiltrated from populated areas. It is known that among other impurities, hydrocarbons (oil) can spread in very large areas with the moving ground water.

Jerbo (1967) has found that methane is being formed during the ageing process of stored quick clay samples. Legget (1973) even maintains that methane can be formed by decomposed organic matter in glacial clay.

#### 5.2.3.2 Acids

Ions of organic acids are of great interest here. The connection between acid peat and varved quick clays indicates the importance in the quick clay forming process of soluble acids, and especially the oxalate ion which is known as a strong dispersing agent is suspected.

By means of paper chromatography, Aleksandrova (1960), studied acids (their ions) present in solutions which were obtained from peat from three places around Moscow and treated with sulfuric acid and extracted with diethylether. She found oxalic, tartaric, citric, malic, lactic, succinic, glutaric and adipic acids. Aromatic acids were protocatechuic and salicylic acids. (She also found amino acids.) Of special interest is the occurrence of oxalate ions.

Wang, Cheng & Tung (1967) investigated the phenolic acids in Taiwan soils and found p-hydroxybenzoic, p-coumaric, vanillic and syringic acids. Nykvist (1963) studied by means of paper chromatography the acid substances present in several Swedish leaf and pine needle extracts. He found malic acid, tartaric acid and phosphoric acids. All these substances disappeared in a few days (not phosphoric acid) both under aerobic and anaerobic conditions. Nykvist states that they are consumed by microorganisms. Lactic acid was formed in his extracts under anaerobic conditions.

Acids present in peat water from southern Belgium have been studied by Ramaut (1955). His isolation method is partly reminiscent of the isolation method used by Berzelius (1833) for crenic acid, but instead of copper acetate Ramaut used lead acetate. He obtained a volatile acid substance with an unpleasant smell. Paper chromatographic examination showed the presence of an acid with  $R_F \approx 0.53-0.54$  (solvent 1-butanol, water, formic acid 100 - 50 - 10). He could not identify this acid.



Ramaut also used a method involving column-chromatographical separation on an active carbon. The method is in principle the same as that used by Forsyth (1947 and 1950). Ramaut isolated a crystalline acid with  $R_F \approx 0.80$  occurring in peat water in very small amounts. The acid is said to be dibasic and he asserts it to be a homologue to succinic acid.

In the beginning of this century, Schreiner and his co-workers (1908 and later) isolated several acid substances from different American soil types. By a method similar to those utilized by Berzelius and Ramaut, but using silver nitrate as precipitating agent, picolin carboxylic acid was isolated. Schreiner et al. (1908a). In another work Schreiner et al. (1908b) isolated dihydroxystearic acid by means of ether extraction. Also other acids were found, such as monohydroxystearic acid, lignoceric acid, "paraffinic acid", etc. Especially interesting is the occurrence of acids such as hydroxystearic acid and lignoceric acids in soils. Substances of this kind can be caused by microbiological natural action in the soil. Such substances, however, can also be directly infiltrated, e.g. from outlets.

Substances of the fatty acid type are also found in peat. If peat is treated with different organic solvents (e.g. ligroin or mixtures of benzene-ethanol of different composition), a brown substance, in peat chemistry called bitumen, is obtained. After saponification this bitumen has dispersing properties.

By means of ethanol it is possible to split up bitumen into one wax part and one resin part (cf. Ch. 7.3.4). The wax part contains, among other things, normal saturated fatty acids and oxy fatty acids. It should be observed that disturbances can occur from impurities.

Work on the analysis of peat bitumen has been made by Sundgrén and his co-workers at the Peat and Oil Laboratory, Helsinki (cf. e.g. Sundgrén & Rauhala, 1949, 1952 and 1957). By means of thin-layer and gas chromatographical methods they have succeeded in isolating and identifying 10 saturated fatty acids in the peat wax. The acid occurring in the highest concentration was lignoceric acid ( $C_{23}H_{47}CO_2H$ ).

The resin part has also been analysed. Titow (1932)

found in the resin two acids with 12 and 14 carbon atoms in the molecule. Rakowski & Edelstein (1932) showed the existence of resin acids with unknown composition.

Kwiatkowski (1965) has tried to analyse several peat resins. In the saponifiable part he found the same fatty acids as in the wax. In the unsaponifiable part he found a great variety of substances.

By treating quick clays in the same manner as has been done with peat, the present Author has found that it is possible to extract bitumen from quick clays and to split it into a wax and a resin part. The wax part contains fatty acids as shown by thin-layer chromatography (cf. Ch. 7.3.4).

These facts show the existence of a hitherto fairly unknown series of frequently natural but often artificial dispersants for clays, viz., soaps, both from fatty acids and resin acids. The dispersing effect from soaps will be shown in Ch.6.

#### 5.2.3.3 Polyphenols

As stated above, Bloomfield (1956) has found that polyphenols can act as dispersing agents in nature. The presence of polyphenols in plants, humus and soils has been examined by Coulson, Davies & Lewis (1960). In most cases they detected the presence of D-catechol and epicatechol as major polyphenols. They also found that these substances could penetrate into the ground and cause a reduction and transporting of iron in the form of complexes (cf. above).

Jerbo (1964) discusses the importance of different tannins. Tannins in humus and soil have been examined by Davies, Coulson & Lewis (1964). They did not find any simple tannins in English soils. The probability of finding such substances in quick clays seems to be small according to the experience that substances of this kind rapidly react anaerobically with the surrounding soil. These high molecular products can, however, be strong dispersants. In Ch. 6, the dispersing properties of some polyphenols and tannins are tested.

#### 5.2.3.4 Other Dispersing Agents

Alcohols. Probably several alcohols occur in quick clays. Nothing indicates that alcohols in free form are effective dispersants. They might, however, form polycondensation products with e.g. amino acids. For this reason the importance of different alcohols ought to be studied.

Esters. The different fatty acids in many cases occur as esters (wax). In sodium clays, saponification reactions, probably due to microbial activity, might occur, giving dispersing soaps. Of course, soap in a clay can originate from infiltration in the ground.

Resins. The resins and the resin acids have been discussed together with fatty acids. As already stated, resins can play a role in the quick clay formation process.

Nitrogen-containing substances. As stated in Ch. 4.3.1, amino acids form very strong dispersing condensation products with carbohydrates, different aldehydes and other substances. Such condensation products can be hydrolysed with acids and the product obtained can be analysed. Aleksandrova (1960) found lysine, asparaginic acid, glycocoll, glutamic acid, threonine, alanine, proline, valine and phenylalanine. The amino acids proper have no dispersing properties as shown in Ch. 6.

Urea is a decomposition product which is able to form polycondensation products with phenols, etc. The substance seems to be of very great interest in the formation of high rapid quick clays.

Ferrochrome lignosulfonates. Complex substances consisting of lignosulfonic acid bound to iron and chromium are at present the dispersing agents most used in the drilling mud industry. As will be seen in Ch. 6, most of the dispersing substances isolated from quick clays and peat contain iron. The iron does not act as a strong coagulant because it is present in the negative ions, as some sort of complex.

#### 5.2.4 Organic Dispersing Substances of Strictly Humic Character

Natural humic substances are known to have strong dispersing properties and have been used industrially for several purposes. It must be noted that only the humus substances with a moderate molecular size have dispersing properties but those with a greater size have cementing properties.

The simplest strictly humic substances existing in nature are, according to Kononova (1961), the crenic and apocrenic acids. Crenic acid or "spring acid" (Swedish "källsyra") was first isolated by Berzelius (1833) from the water of the old Porla Mineral Spring<sup>1)</sup>. Berzelius found that through atmospheric oxidation crenic acid is converted into brown, sparingly soluble substances, apparently resembling humic acids, which are termed apocrenic acids, sedimentary spring acid.

Berzelius' experience is of great interest because it seems to be the first paper mentioning what is called ageing effect today. His paper is quite in accordance with modern literature which states that clay ageing largely depends on changes in the organic material (cf. Jerbo, 1967).

Berzelius claims to have isolated the purest form of crenic and apocrenic acids from ochre from the Porla Spring as follows. The ochre was boiled with a potassium hydroxide solution for about 1 hour. The solution was filtered and acidified by means of acetic acid and the apocrenic acid was filtered and acidified by means of acetic acid. The apocrenic acid was then precipitated by means of copper acetate and filtered off, the filtrate neutralized by means of ammonium carbonate and the crenic acid precipitated with copper acetate. The resulting copper crenate had a grey-green colour. Thereafter it was washed, dispersed in water and decomposed with hydrogen sulphide. The copper sulphide was filtered off and the filtrate contained the crenic acid. The solution is a pale-yellow liquid

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<sup>1)</sup> The present commercial "Porla Table Water" is not taken from this old spring, which Berzelius and the present Author have analyzed.

unstable in air. After evaporation a pale-yellow amorphous mass remains having acidic properties and no smell. Like most humic substances, crenic acid in later years has been given another meaning, viz., substances which are extracted from the soil by sodium hydroxide but not precipitated by acidification. The difference between crenic acids and fulvic acids is very diffuse. In the present paper, the term crenic acid is given its original meaning, i.e. acids of the same chemical nature as those isolated by the method used by Berzelius on water or ochre from the Porla Spring. If similar acids are isolated from soils or water they are referred to in this paper as crenic acids, but if they have other chemical characteristics this designation is not used.

Being a relatively low-molecular substance, crenic acid seems to be able to form salts with dispersing properties and to take part in the natural dispersing reactions. Also its tendency to age and form more high-molecular gel aggregates is well in accordance with the properties noted on natural quick clays. Hitherto (1974) it has not been possible to obtain a clear picture of the structure of crenic acid.

Several authors have tried to split up the humic acids into groups according to their solubility. Odén (1919), for instance, distinguished between fulvic acids,<sup>1)</sup> hymatomelanic acids and humic acids. The fulvic acids are the water-soluble acids, especially the acid substances in peat water. The term fulvic acid gradually changed its meaning. Many authors use the term for acids which are extracted from the soil by alkali but not reprecipitated from the solution by mineral acids. As will be seen from the present work, fulvic acid isolated in this way has quite a different composition to that of the acids isolated from peat water. Since peat water contains crenic and apocrenic acid, the conception fulvic acid includes the crenic

acids and probably other more complicated water soluble acids.

Substances of the fulvic acid group are of great interest in this connection for the same reason as mentioned for crenic acid.

The hymatomelanic acids are the alcohol-soluble part of the acid humus precipitate. As shown in Ch. 6 in this report, hymatomelanic acids are strong dispersants for clays and hence they are of interest here. Many authors (e.g. Odén, 1919) have regarded hymatomelanic acid as a compound possessing a number of specific properties such as solubility in water, alcohol and alkali, a carbon content of 62% and an equivalent weight of 250.

A different point of view was expressed by Shmuk (1924 and 1930). He regards the hymatomelanic acids as mixtures of chemically individual components of the resin acid type. Shmuk isolated and identified in the alcohol soluble fraction of humic acids a number of resin acids differing in melting point and elementary composition.

Resinates are dispersants for clays and therefore Shmuk's work is of interest. Resin acids are also present in the products isolated by among others Sundgrén & Rauhala (1949) from peat. As will be seen later in this report it is possible to show the presence of a fatty acid fraction, a resin acid fraction and a fraction of more complicated compounds in hymatomelanic acid. Condensation products between aminoacids and other substances, e.g. carbohydrates or polyphenols, also seem to be present.

Humic acid is the non-water, non-alcohol soluble part of the humus substances soluble in sodium hydroxide. Also the humates have strong dispersing properties as mentioned before and have found practical application in the drilling mud industry. These substances have a complicated structure and must be regarded as a kind of polycondensation products.

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<sup>1)</sup> Fulvic acid means yellow acid.

## 6. LABORATORY STUDIES ON DISPERSING AGENTS. TESTING PART

### 6.1 General

In this chapter the possibility of transforming non-quick clays into quick clays of different rapidity will be investigated. Also the possibility of changing the rapidity number of a quick clay by chemical means will be studied. A very important part is to study whether non-quick clays sedimented in different environments can be transformed into quick clays by changes not affecting the grain skeleton proper, i. e. whether both fresh-water sedimented and salt-water sedimented clays can become quick by a simple alteration of the chemical bindings in the system.

Some studies of the dispersing effect of substances expected to take part in the natural processes forming quick clays will also be made.

### 6.2 Dialysis Studies on Quick Clay Formation

As typical reference clay, varved fresh-water sedimented clay from Räcksta (some 15 km NW of central Stockholm) and from Jordbro (40 km S of Stockholm) was selected. Pieces of standard piston samples, about 6 cm in height and 5 cm in diameter, were placed in solutions (1%) of different dispersing agents. The common geotechnical properties ( $H_1$ ,  $H_3$ , etc) and the change of the chemical composition of the pore water were determined before and after the experiment.

It was found, as seen in Table 1 that it is possible to transform varved clays with normal sensitivity into quick clays in common meaning (high sensitive clays) by treating them with dispersing agents. It is remarkable that the high-molecular macromolecules easily penetrate into the clay samples.

All dispersing agents seem to influence the geotechnical properties in different ways. In all cases there is a decrease in the  $H_1$ -value and in the  $H_3$ -value as obtained from the fall-cone test. Ferrochrome lignosulfonate and sodiumpyrophosphate reduce the  $H_1$ -

value to the lowest in the scale (0.33). There seems to be no systematic connection between changes in the water content during the experiments and changes in the strength values. The  $H_1$ -values can decrease considerably when samples are treated with water glass and ferrochrome lignosulfonate in spite of the fact that the water content decreases at the same time. For sodiumpyrophosphate there was, on the other hand, an increase in the water content.

The rapidity number increased in all cases, except for the treatment with water glass where a very low-rapid quick clay with (after a great amount of stirring) the lowest  $H_1$ -value (0.33) in the scale was obtained.

The properties of this "quick clay" were similar to those of many natural low-rapid quick clays. By stirring this type of clay a granular mass was formed first. Individual "granules" could then, by intensive stirring, be transformed into a liquid mass.

A typical change of pore water composition by the dialysis treatment is seen in the chromatogram Fig. 11, page 17. Here the divalent cations have been precipitated or complex bound by the dispersing agent.

### 6.3 Studies on the Dispersing Properties of Different Substances

#### 6.3.1 General

A very simple method was used in order to test the dispersing properties of different substances. 100 g of kaolin 46<sup>1)</sup> suspended in water and having an  $H_1$ -value of 10 (about 240 g kaolin per 100 ml water) was remoulded and its  $H_1$ -value, electrical conductivity, pH-value and chemical composition of its pore water were determined. Then 0.1 g of the dispersing agent to be tested was added. After remoulding the proper-

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<sup>1)</sup> Kaolin 46 was used as a well defined clay material (Söderblom, 1969), because it is only the relative influence of different substances which is to be tested.

ties mentioned above were determined again. (Pore water composition was determined in a special test in which the clay was treated in such a way that it obtained its minimum value.) The process was repeated for 0.2, 0.3, 0.5, 1.0, 1.5 and 2.0 g of the dispersing agent per 100 g of clay.

In Ch. 4 it was said that both inorganic and organic substances could be dispersing agents. Since a systematic examination of all pertinent substances and a survey of their dispersing properties would be an immense task, the present investigation had to be limited to include only the more common substances suspected to be active, according to experiences and literature studied.

### 6.3.2 Inorganic Dispersing Agents

Because the quick clays are slightly alkaline and have sodium as dominating cation in the pore water, the effect of sodiumhydroxide was first studied. The result is shown in Fig. 12. This substance has only a small influence on the remoulded strength of the kaolin used.

As typical inorganic dispersing agents, sodium diphosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ), sodium orthophosphate  $\text{Na}_3\text{PO}_4$ , commercial water glass and sodium silicate ( $\text{Na}_2\text{SiO}_3 \cdot 9 \text{H}_2\text{O}$ ), according to Vesterberg (1914), were chosen.

The dispersing properties of sodium diphosphate are shown in Fig. 13. As could be expected it has a very strong dispersing effect. The corresponding effect of sodium orthophosphate is somewhat weaker. The result from the test with water glass, being a strong dispersing agent, is shown in Fig. 14. The Vesterberg silicate has a weaker effect.

### 6.3.3 Organic Dispersing Agents of Individual Nature

In the case of organic dispersing agents of "individual nature" it is possible to use definite model substances as given below.

Carbohydrates. Experiments were made with galacturonic acid, cane sugar and saponine. Experiments

with polymerisation products of carbohydrates will be described together with humic substances (Ch. 6.3.4).

The results from neutralized galacturonic acid ( $\text{pH} \approx 8$ ) and cane sugar are shown in Table 3. It is seen that untreated cane sugar has no dispersing properties and that sodium galacturonate has only a moderate effect.

The result with saponine is shown in Fig. 15. As expected, the dispersing effect was good.

Acids. A few examples of sodium salts of simple organic acids were tested, viz., oxalic, malic, lactic and succinic acids<sup>1)</sup>. The results are shown in Table 3. Only sodium oxalate showed strong effect which also is expected from the insolubility of calciumoxalate. As salts of higher fatty acids, toilet soaps were tested and also sodium stearate, sodium hydroxy stearate and sodium oleate (purity: Kebo puriss).

The result from toilet soap is shown in Fig. 16. It is seen that a certain amount of substance must be added before the dispersing effect becomes apparent, as is shown in the figure. The remaining part of the curve is similar to that obtained by the other strong dispersing substances (sodium pyrophosphate, etc.) and has no similarity to that obtained by saponine.

The results from pure soaps, sodium stearate and sodium oleate are shown in Figs. 17-18. It is seen that sodium stearate has a small effect but that sodium oleate is a good dispersing agent.

The dispersing curve obtained from saponified bitumen from Rosshyttan is shown in Fig. 19. This curve differs markedly from that obtained from soap. Also in this case the effect was less than that obtained with the strong dispersing agents, e.g. sodium pyrophosphate. It is probable that this material contains other dispersing substances beside fatty acids.

Resins. At present it seems not possible to get model substances corresponding to the typical resins occurring in quick clay and peat.

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<sup>1)</sup> It must be stressed that substances of this kind are not stable in soil as found by, e.g., Wang et al. (1967).

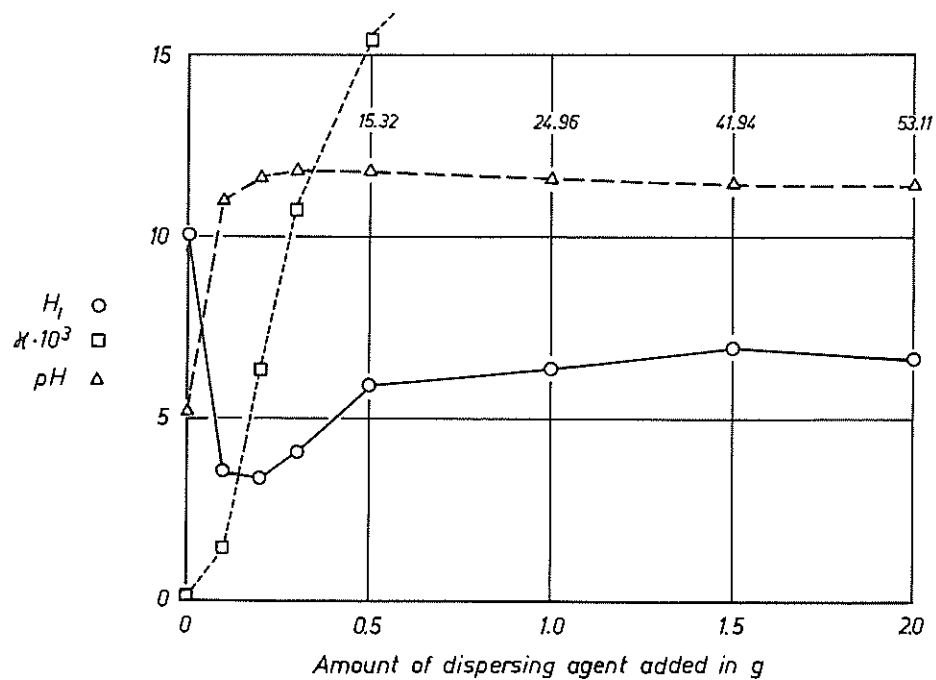


Fig. 12 Influence of sodium hydroxide on the remoulded shear strength of kaolin and on its pH-value and conductivity ( $\kappa$  given in  $\text{ohm}^{-1}\text{cm}^{-1}$ )

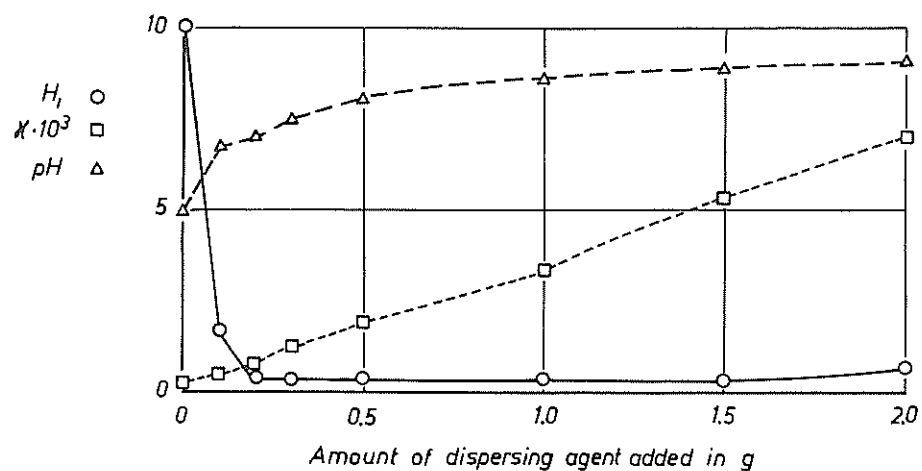


Fig. 13 Influence of sodiumdiphosphate on the remoulded shear strength of kaolin and on its pH-value and conductivity

Table 3 Examination of the dispersing properties of different well-defined substances.  
In the case of acids, the sodium salts have been studied

Chemical group	Substance	Max. decr. of $H_1$ -value %	Disp. agent causing max effect in g/100 g clay
Inorganic	Sodium ortho-phosphate ( $Na_3PO_4 \cdot 12 H_2O$ )	89.0	1.0
	Sodium silicate acc. to VESTERBERG, 1914	72.9	2.0
Carbohydrates	Galacturonic acid	58.0	2.0
	Cane sugar	No effect	-
Organic acids	Oxalic acid	92.0	0.5
	Malic acid	83.0	1.0
	Lactic acid	49.0	2.0
	Succinic acid	59.0	1.0
Amino acids	Valine	Coagulates	-
	Alanine	Coagulates	-
	Glutamic acid	Coagulates	-
	Urea	Coagulates	-
Lignosulfonates	Sulfite liquor	90.2	10.0
	Vafex	89.0	10.0
Polyphenols	Resorcin + NaOH	Coagulates	-
	Gallic acid + NaOH	96.7	0.5
	Quinone + NaOH	96.7	0.3
Natural substance	Humic acid, EGA-Chemie AG	96.7	0.3

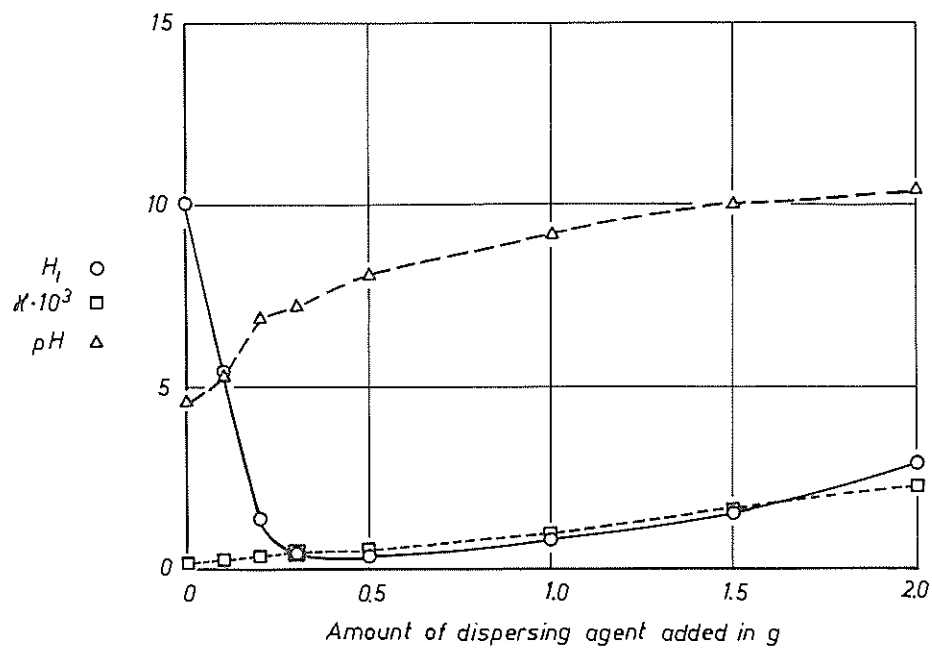


Fig. 14 Influence of water glass on the remoulded shear strength of kaolin and on its pH-value and conductivity

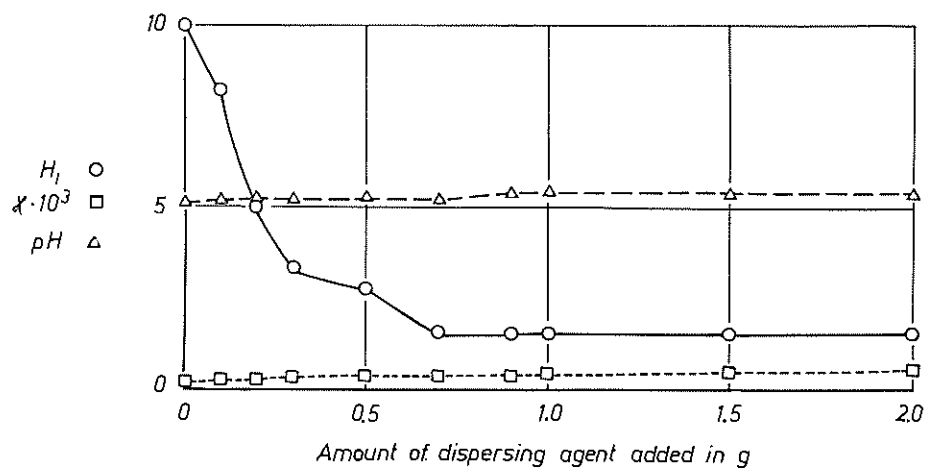


Fig. 15 Influence of saponine on the remoulded shear strength of kaolin and on its pH-value and conductivity

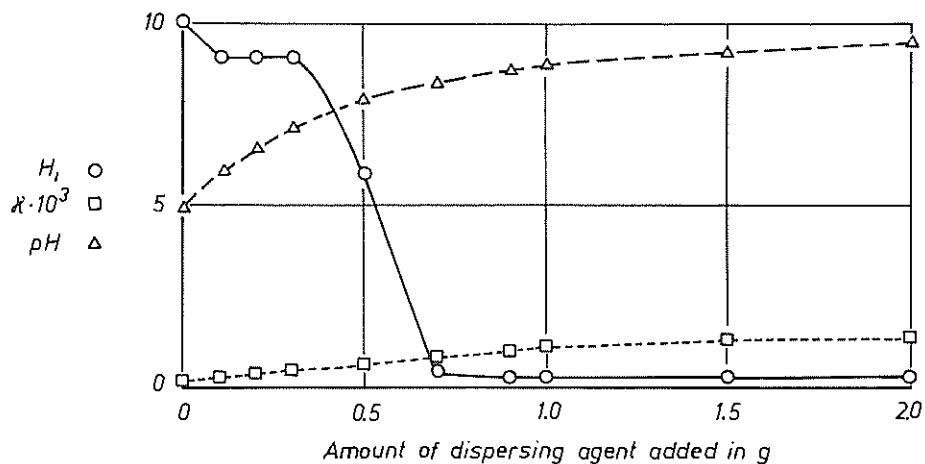


Fig. 16 Influence of toilet soap on the remoulded shear strength of kaolin and on its pH-value and conductivity



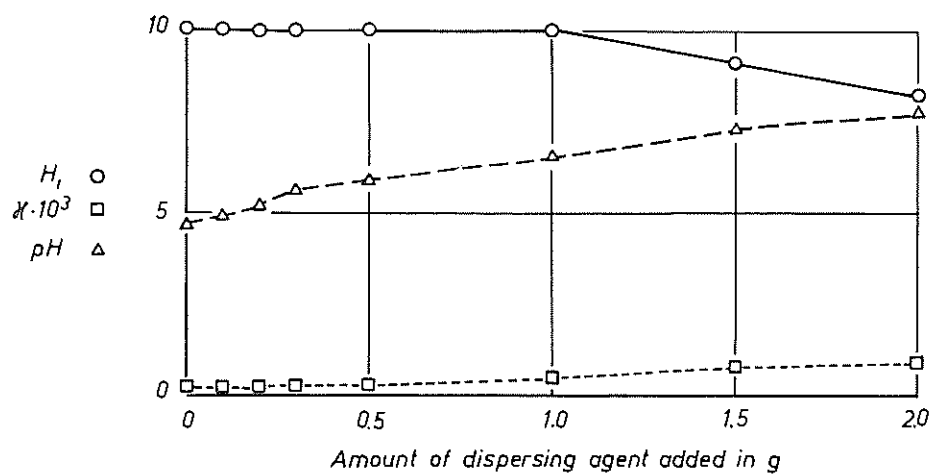


Fig. 17 Influence of sodium stearate on the remoulded shear strength of kaolin and on its pH-value and conductivity

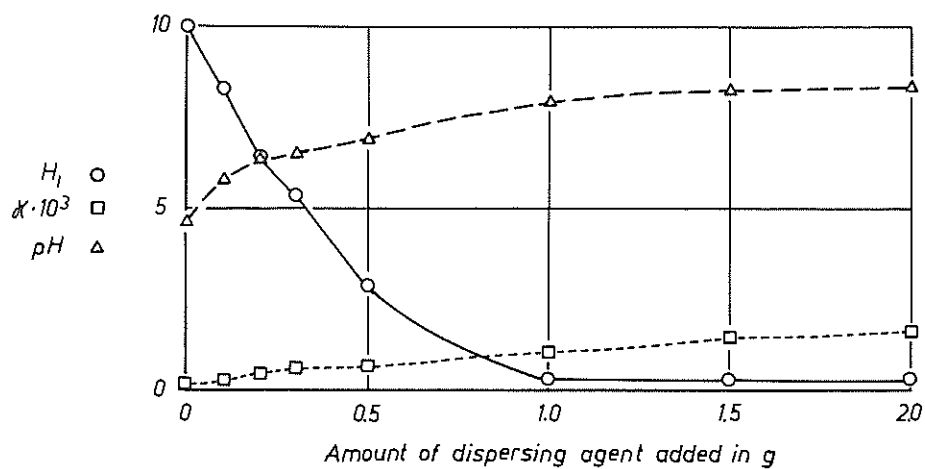


Fig. 18 Influence of sodium oleate on the remoulded shear strength of kaolin and on its pH-value and conductivity

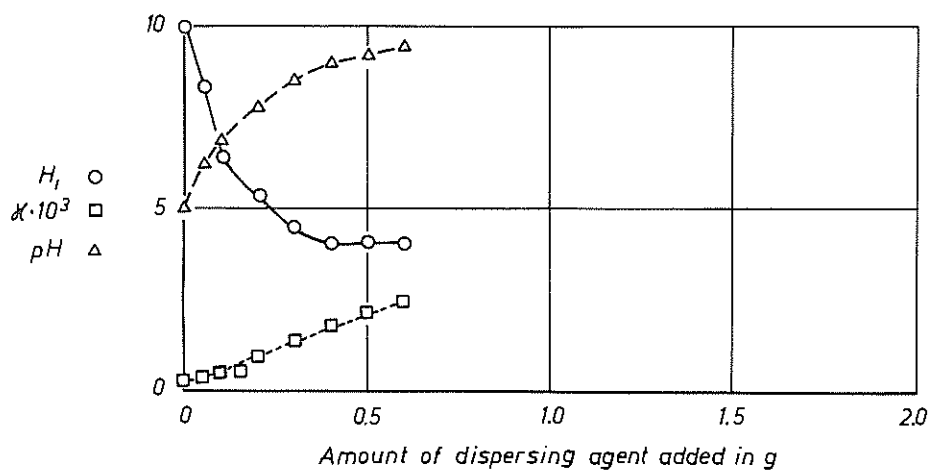


Fig. 19 Influence of saponified bitumen from peat from Rosshyttan on the remoulded shear strength of kaolin and on its pH-value and conductivity

Nitrogen-containing substances. Three amino acids were tested, viz., alanine, valine and glutaminic acid. Condensation products of amino acids are reported in connection with humus substances below. The dispersing properties of urea were also determined.

The results from the amino acids are shown in Table 3. No dispersing effect was noticed for any of the substances examined. On the contrary, the clay became somewhat stiffer. The effect of urea is lacking.

Two commercial drilling mud thinners being "ferrochrome lignosulfonic acid" (commercial name Lignite and Lignosite) were investigated. Waste sulfite liquor and a lignosulfuric acid preparation called "Vafex" were studied. Iron lignosulfonic acid was prepared from waste sulfite liquor and iron chloride and from "Vafex" and iron chloride. These substances are strong dispersing agents as shown in Fig. 20. Sulfite lignor and "Vafex" have a weaker effect. Iron lignosulfonates from sulfite liquor and from "Vafex" have a good effect.

Polyphenols. High molecular condensation products of phenolic substances were studied. Hydroquinone, quinone, tannic and gallic acids were dissolved in 0.1N NaOH-solution to saturation and the solutions evaporated. By this treatment easily soluble humic-like dispersing substances were obtained. Resorcin was also examined.

The results from the condensation products are shown in Figs. 21-22 and Table 3. Resorcin does not give humic-like polycondensation products and has no dispersing properties, but air-oxidised NaOH-treated hydroquinone and quinone are very good dispersants. The same is the case with gallic and tannic acid, which also form easily soluble humic-like substances in slightly alkaline solution.

#### 6.3.4 Humic-Like Substances

Commercial humic acid (EGA Chemie AG) was chosen as a model for "strictly humic substance". Hymatomelanic acid was prepared from peat from Rosshyttan in accordance with a method described by Odén (1919). The humus precipitate was made as

in Ch. 7.3.2. It was dried and boiled for four hours with an excess of 95% ethanol. The brown solution obtained was evaporated giving hymatomelanic acid. As shown in Fig. 23 its ions have a very strong dispersing effect. Humic acid neutralized with NaOH to  $\text{pH} \approx 8$  is also a very strong dispersing agent.

Evaporation residue from Rosshyttan peat was also examined qualitatively. It had relatively good dispersing properties. A series of qualitative examinations was also made on different peat acids isolated according to Ramaut (cf. Ch. 7.3.3), and the results are shown in Table 5. These acids have been discussed together with the humic substances because considerable parts of them belong to this group. But as shown they may also contain a considerable amount of resin acids.

Standard melanoidin according to Enders & Theis (1938) (cf. Ch. 2.3.3) was investigated. The result is shown in Fig. 24. It has a very strong dispersing effect.

## 6.4 Discussion of Test Results

Experiments showing the ability of organic material to give a nodule structure of synthetic quick clay like that occurring in nature have already been treated and discussed in Ch. 4.2. It is questionable whether there is any possibility of explaining the formation of quick clay with a natural structure without taking the influence of organic material into consideration.

An interesting result was obtained in the dialysis experiment with water glass. A quick clay with probably cementated structure and with a low rapidity number was obtained in a short time.

As shown in the dialysis experiments (Ch. 6.2) high molecular substances can easily penetrate into the clay samples, in some cases with a reduction of the strength ( $H_g$ -value). It is probable that forces other than the Brownian movements usually active in the diffusion processes have acted in this case. The diffusion rates are abnormal with respect to the transmission factors for the high molecular ions.

Dialysis experiments have shown, that even fresh-

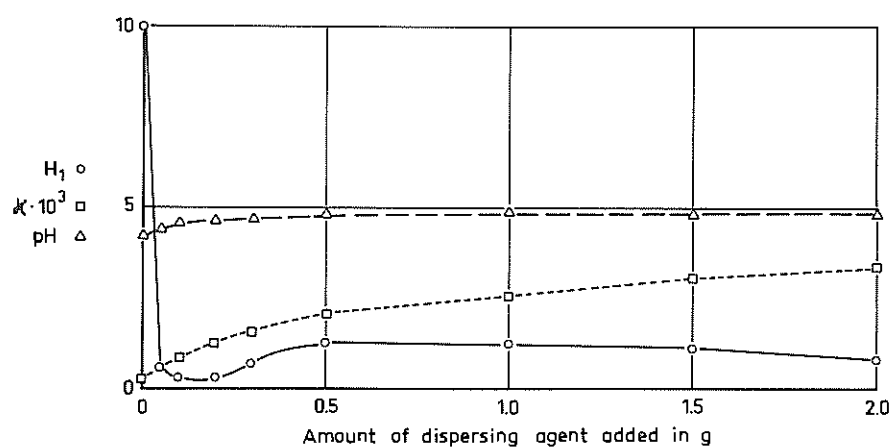


Fig. 20 Influence of lignite on the remoulded shear strength of kaolin and on its pH-value and conductivity

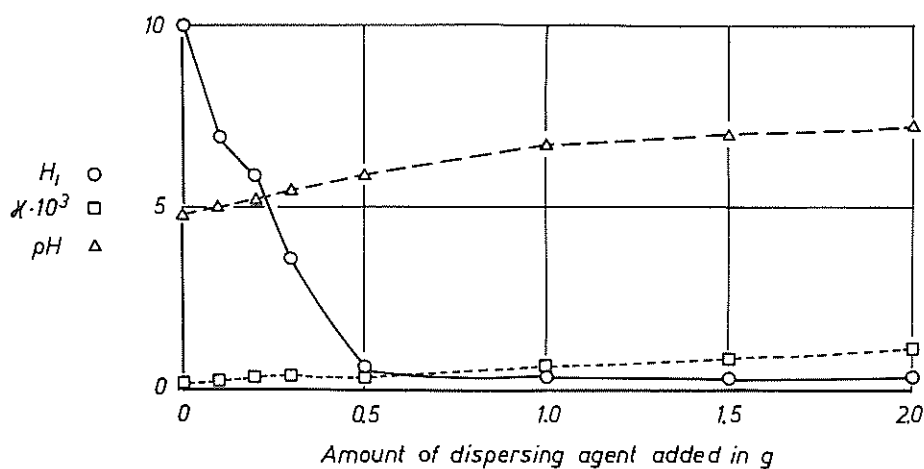


Fig. 21 Influence of hydroquinone slightly alcalized with NaOH on the remoulded shear strength of kaolin and on its pH-value and conductivity

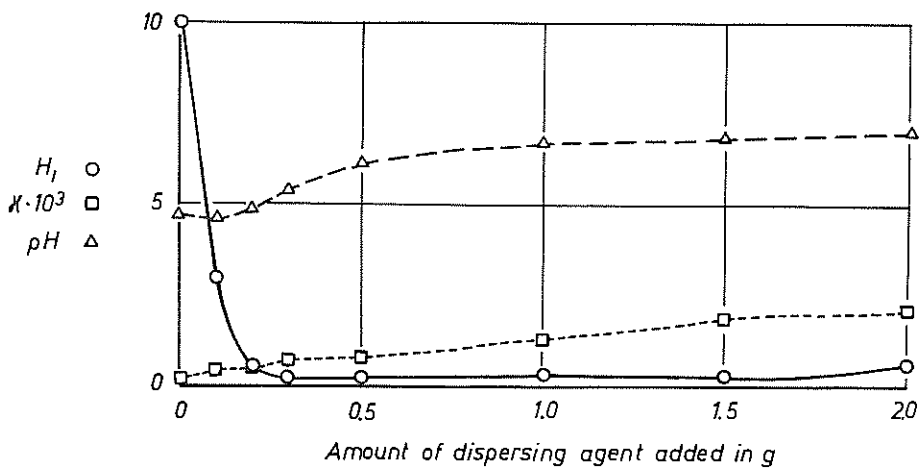


Fig. 22 Influence of sodium tannate on the remoulded shear strength of kaolin and on its pH-value and conductivity

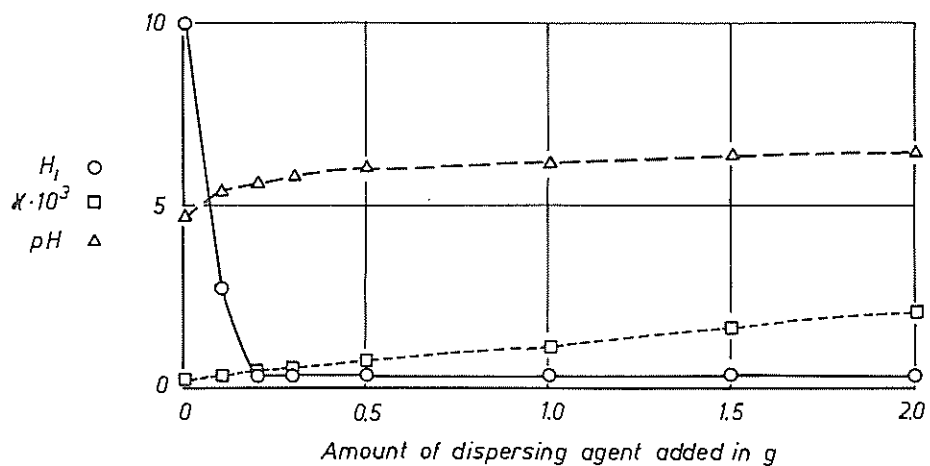


Fig. 23 Influence of sodium hyalomelinate on the remoulded shear strength of kaolin and on its pH-value and conductivity

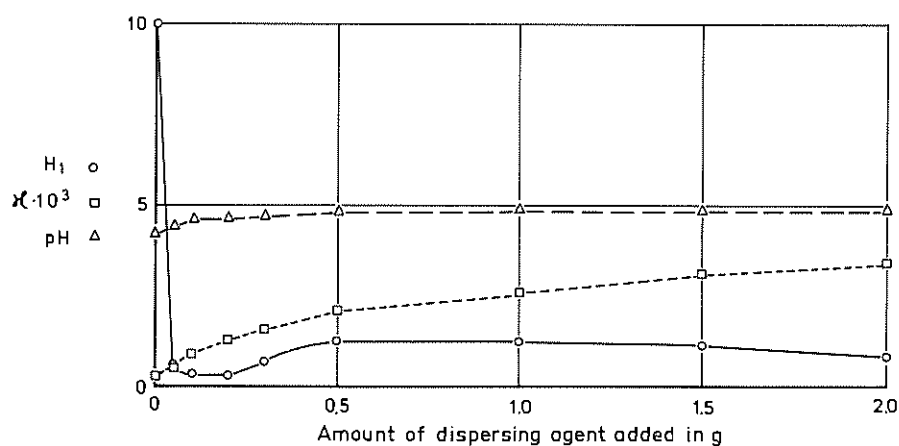


Fig. 24 Influence of standard melanoidin neutralized to pH 8 on the remoulded shear strength of kaolin and on its pH-value and conductivity

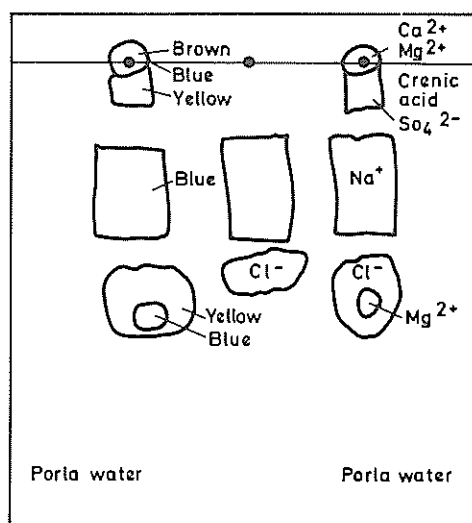


Fig. 25 Small-paper chromatogram showing the ionic composition of water from Porla

water sedimented clays can be transformed into quick clays through suitable treatment. This is also in accordance with the observations that the sensitivity curve in a quick clay profile containing both varved and non-varved (marine) quick clays does not as a rule show any irregularities in the transition between the different clay types.

It also tallies with the observations that varved and non-varved clays have a module structure as described in Ch. 4.2.

Another purpose of the testing part of the investigation was to obtain some knowledge of the occurrence of dispersing agents in different groups of chemical substances, thus giving an indication of what types of substances should be looked for in the analytical part in Ch. 7 of the present work. Dispersing agents occur in most of the examined groups among both the inorganic and organic substances. It does not at present seem possible to find any relation between the chemical structure of a substance and its dispersing properties. It can, however, be concluded that the dispersing substances with a few exceptions, e.g. the saponines, can bind calcium and magnesium ions in complex form. The mechanism is, however, so far unknown.

As shown in Fig. 14 some soluble silicates have strong dispersing properties. A small content of such a substance in a clay will make it highly sensitive and also affect its rapidity number. Silicates of this type can be expected to play an important role in the formation of quick clays, but no chromatographic methods are available for soluble silicate ions. At present it is not possible therefore to examine the composition of possible soluble silicates in the clay. Artificial quick clays can easily be prepared in the laboratory, however, by means of soluble silicates (cf. Table 1). It is also possible to study the presence of silicate in the impure infiltration water that is expected to take part in the quick clay forming process.

As reported by, e.g., van Olphen (1965), the peptizing effect is not only an effect of pH-changes and ion exchange. This was also confirmed by the Author's experiments with sodium hydroxide. But as stated earlier (Söderblom, 1969) quick clays always have sodium as the dominating cation in their pore water.

In some cases, however, a strong dispersing effect of sodium hydroxide on kaolin was noticed. This is according to van Olphen (1965) particularly true when the kaolin clay shows an acid reaction. In such cases dispersing acids are often present in the clay. They are neutralized by the added alkali and the ions thus formed frequently act as peptizing chemicals.

It is thus obvious that ions of organic acids in general, especially oxalic acid, are substances which can be strongly suspected as taking active part in the quick clay process. Therefore part of the analytical work below has been devoted to examining the content of soluble acids in quick clays and peat water.

The strong dispersing properties of humic acid and the extremely strong effect of hymatomelanic acid make it clear that clay dispersing agents with a strong effect do exist in nature and can be formed by natural processes. In addition, all dispersing agents which are infiltrated in the ground from outlets etc. should be studied. Thus a complete solution of the quick clay problem must also include a determination of the chemical structure of the humic acids. The general knowledge in this respect is, as said above, very limited.

The experiments on melanoidin have, however, given some hints on the composition of dispersing humus substances and as will be seen in Ch. 7.4 one can by acid hydrolysis obtain some information on the "building stones" of humic dispersing agents. The similarity between the dispersing curves of hymatomelanic acid and oxydation products of hydroquinone and quinone may indicate quinoidic polycondensation products as very strongly acting dispersing substances, but the lack of suitable chromatographic methods for quinoidic substances makes it at present impossible to analyze them.

Condensation products containing iron are also of interest. Most of the dispersing agents occurring in nature contain iron, which as seen in Ch. 7.2.3, is a part of the negative ions.

Amino acids as such are not dispersing agents, but condensation products containing amino acids have very strong dispersing action. Therefore one must

search for amino acids and for substances able to polymerise with such acids.

In Table 2 urea was classified as being a strong dispersing agent. In the present experiments, Table 3, no dispersing effect was found for the pure preparations used. Technical preparations may show a dispersing effect because urea-like polyphenols can give polycon-

densation products with a strong dispersing action.

Synthetic detergents, water softeners and similar products have, as might be expected, a strong dispersing effect. Because such substances have only been generally used for about 20 years, a quick clay containing such substances must be of rather late origin.

## 7. LABORATORY STUDIES ON DISPERSING AGENTS. ANALYTICAL PART

### 7.1 General

A complete analytical study of the importance of the organic material to quick clay formation must include materials with a cementing effect, materials with the ability to form nodule structures and materials with dispersing properties.

As mentioned in Ch. 5.2 the cementing organic materials are believed to be very high-molecular gels with complicated composition. An analysis of their composition seems to be impossible to perform with present techniques and is also outside the scope of this report. The same is true of the materials forming the fissured structure discussed above.

The dispersing organic substances are of moderate molecular weight as mentioned in Ch. 5.3 and might possibly be analysed with success. Due to this fact this analytical part is limited to substances of this kind.

The analytical work has been divided up. In the first part (Ch. 7.2) the examination starts with a study of typical water-soluble substances. In the second part (Ch. 7.3) other possible dispersing substances were studied, and in the third part supplementary studies and a critical examination are made.

### 7.2 Studies of Water-Soluble Substances

#### 7.2.1 Separation with Ion Exchangers

The method used by Nykvist (1963) and others was first employed to determine water-soluble compounds present in peat water and quick clays. (This method is a standard method used for the study of biological fluids.) Filtered natural water was first allowed to pass a cation exchanger column IR 120  $H^+$  at a rate of 0.5 ml per min. The column was washed with distilled water until all anions (organic and inorganic) and non-ionic substances, e.g. carbohydrates were removed. The cations were eluted with 400-500 ml 1N  $NH_3$ . The eluate was evaporated in vacuo at 40°C. The solution that had passed through the cation exchanger was then allowed to pass a column of anion exchanger resin IRA 410  $CO_3^{2-}$  at the same rate. The column was washed with 300-400 ml distilled water that carried the non-ionic solution and after that the anions were eluted with 400-500 ml 1N HCl. The solution of non-ionic substances and the solution of anions were also evaporated at 40°C in vacuo. The three evaporates were dissolved in 1-4 ml distilled water. 1-30  $\mu$ l of these concentrated solutions were analysed by paper chromatography.

### 7.2.2 Paper Chromatography

The solutions obtained were subjected to paper chromatography. Paper Whatman 1 was used. In most cases the unknown substances were analysed in four concentrations, 30, 21, 12 and 3  $\mu$ l. As the migration of a substance often is dependent on its concentration, it was found suitable to give the complete chromatograms. Standard substances were run parallel to the unknown substances. Standards used and the deviations from the above-mentioned concentrations are given in the captions of each chromatogram. The  $R_F$ -values of the standards are taken from Linskens (1959).

Organic acids were subjected to chromatography with the solvent system butanol-formic acid-water (4-1-5) (Linskens, 1959). The butanol phase is used as eluting liquid and the formic-acid water phase was used to saturate in the chromatographing vessel. Different developers were used, in most cases bromophenol blue. The organic acids were also studied in the same system as for inorganic acids.

Inorganic acids were chromatographed in the solvent system ethanol - ammonia(0.94) - water (80-16-4) as described by Söderblom (1969).

Inorganic cations were studied either in the same system as the acids or in the solvent system ethanol-4n acetic acid (80-20) (cf. Söderblom, 1969). The cations were made visible either with bromophenol blue or with violuric acid.

Amino acids were analysed in the solvent system butanol-acetic acid-water (4-1-5) (cf. Linskens, 1959) and developed by ninhydrin. Comparative chromatograms were also performed in the solvent system used for organic acids.

Sugars were analysed in the solvent system butanol-acetic acid-water (4-1-1). The chromatograms were sprayed with ammoniacal silvernitrate solution.

Polyphenols were studied in the solvent system butanol-formic acid-water (4-1-5) in butanol-acetic acid-water (4-1-5) as proposed by Linskens (1959) and in acetic acid-water (2% acetic acid). Polyphenols were detected by dipping the paper in a solution of 1%  $\text{FeCl}_3$

and 1%  $\text{K}_3\text{Fe}(\text{CN})_6$  and a subsequent washing with water.

Some special reagents were also employed. Ammonium molybdate-perchloric acid-tin (II) chloride was used to detect phosphoric acid (also organic phosphoric acids). All such acids are transformed by the perchloric acid to orthophosphoric acid. The different acids differ in  $R_F$ -value (Waldi, 1955). Isatin was used to detect amino acids (Linskens, 1959) and phenol-sodium hypochlorite to detect urea (Block et al., 1958). Inorganic cations were developed with violuric acid (Seiler et al., 1952).

### 7.2.3 Examination of Water from Porla and Morsta

The water from these two places seems to be unaffected by any form of impurity and seems to represent "pure natural water".

The water was firstly examined untreated with the small-paper method described by Söderblom (1969). The result is seen in Fig. 25, page 35. Chloride and sulfate ions are present in both water samples and more complicated ions, probably organic.

About 5 l of Morsta water was concentrated in a pyrex vessel in vacuo at 40°C to 250 ml and treated in the ion exchangers. In a parallel sample, 5 l of water was percolated through the ion exchangers at a rate of about 2 ml per min. Both treatments gave, as seen below, the same results and for this reason the more rapid method with direct percolation of the water was chosen in the following studies. The different eluates were first treated in the same way as said above. The same experiment was also made with water from the spring at Porla in order to get some information on the crenic acid. Dispersing experiments were made with all evaporated eluates.

The small chromatograms from the anion eluate showed a considerable amount of chloride ions. Also sulfate ions were present. A remarkable fact was that also sodium and calcium ions could be detected in the eluates.

The chromatogram for anions in the Morsta water is shown in Fig. 26. None of the wellknown acids, such as oxalic, malic, tartaric acid, could be found (cf. Nykvist, 1963). Three or sometimes four acids with low  $R_F$ -values from 0.03 to 0.45 (App. 3) could be distinguished. Disturbances in the chromatogram can have been caused by the chloride and sulfate ions occurring in the water (cf. small-paper chromatograms in Fig. 25). Spraying with ninhydrin indicated the presence of amino acids in the anion eluate.

Spraying with the molybdate reagent for phosphoric acid gave negative results. Development with  $\text{FeCl}_3\text{-K}_3\text{Fe(CN)}_6$  gave a weak positive reaction on the acid with the lowest  $R_F$ -value shown in Fig. 26. Spraying with potassium rhodanide solution gave two red spots indicating the presence of complex bound iron anions.

A small-paper chromatogram with the untreated water gave no spot with KSCN, but the spot absorbing ultra-violet light indicated that iron was very hard complexly bound.

A qualitative test with ammoniacal silver nitrate solution showed that small amounts of carbohydrates were present. The two iron spots (cf. above) gave a strong absorption of ultraviolet light.

This study thus gave the following result. Acid substances of the type of condensation products of phenols, amino acids, carbohydrates and iron seem to be a main constituent of the organic substances in peat water. Like the ferrochrome lignosulfonates, substances of this kind have clay dispersing properties. These substances are decomposed by the treatment in the ion exchanger, the eluate containing  $\text{Fe}^{3+}$ -ions (easy to show with KSCN). A test on the cation eluate with ninhydrin gave a somewhat fuzzy result. One could possibly observe  $\alpha$ -alanine. The small-paper chromatogram showed no sodium or calcium ions. A chromatogram of the non-ionic eluate gave a negative result for reducing sugars. The chromatogram of phenols, developed in 2% HAc and sprayed with 1%  $\text{K}_3\text{Fe(CN)}_6$  is shown in Fig. 27. No simple polyphenols could be detected, but substances with probably very complex structure and having high  $R_F$ -values (at lower concentrations closely following the

solvent front) were detected.

The result from the Porla water was similar to that obtained from the Morsta water. The acid substances are seen in Fig. 28. Also in this water the small-paper chromatograms showed the presence of chloride and sulfate ions.

#### 7.2.4 Examination of Quick Clays

One of the greatest difficulties in examining the quick clay is to separate from the clay the adsorbed substances without disturbing their structure. As stated by Söderblom (1969) the natural dispersing agents in quick clays and the dispersing agents added to kaolin, were not removed by treatment with salt and a strong subsequent dialysing. This indicates strong adsorbing forces (chemisorption), and the possibilities of extracting the adsorbed substances from the quick clay in unchanged form therefore seem to be small. Thus, mild treatment is not efficient in removing the dispersants and a strong solvent might disaggregate them.

There are, however, in some cases possibilities of approaching the problem. Substances of the kinds in question sometimes occur in more or less excessive amounts in some clays and in such a case it should be possible to remove them by suitable treatment.

Humic substances are usually extracted from a soil by means of sodium hydroxide solution. This solution generally dissolves a brown-yellow substance from quick clays. If treated with alcohol, substances with very strong dispersing properties are obtained. Sodium hydroxide, however, attacks the clay minerals.

The peat researchers have in recent years shown that different organic solvents can extract almost unchanged substances from peat and the same may be expected to apply in the case of quick clays. Coulson, Davies & Lewis (1960), among others, used ethyl acetate to extract polyphenols from different substances. During the present investigations it was found, however, that ethyl acetate only extracts from clays such organic substances as lack dispersing effects. Acetone-water, especially 90% acetone - 10% water, has been shown



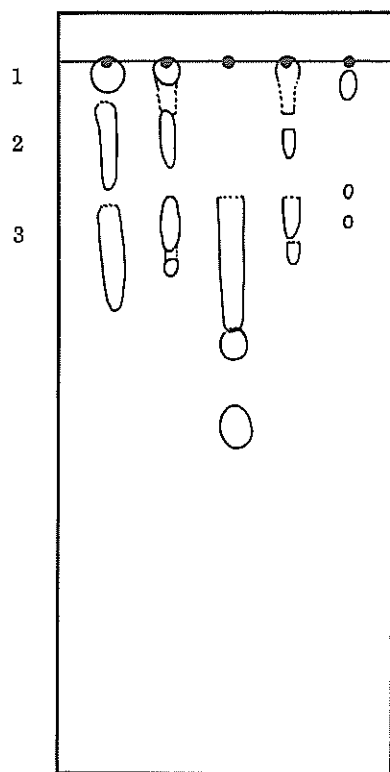


Fig. 26 Paper chromatogram showing anions in Morsta water

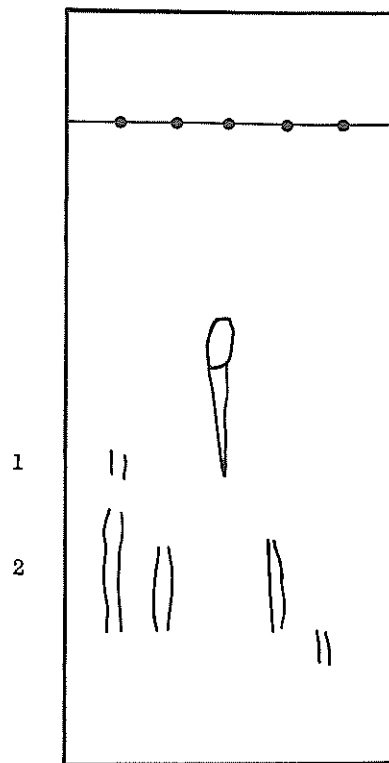


Fig. 27 Paper chromatogram showing quick clay extract from Rosshytan (left) and phenols in Morsta water (right)

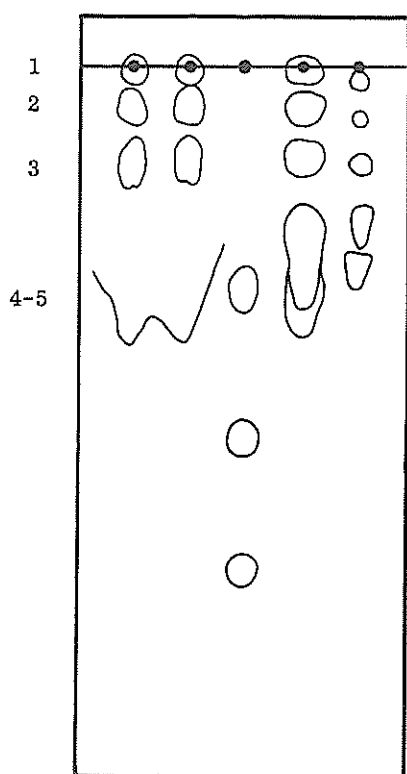


Fig. 28 Paper chromatogram showing anions in Porla water

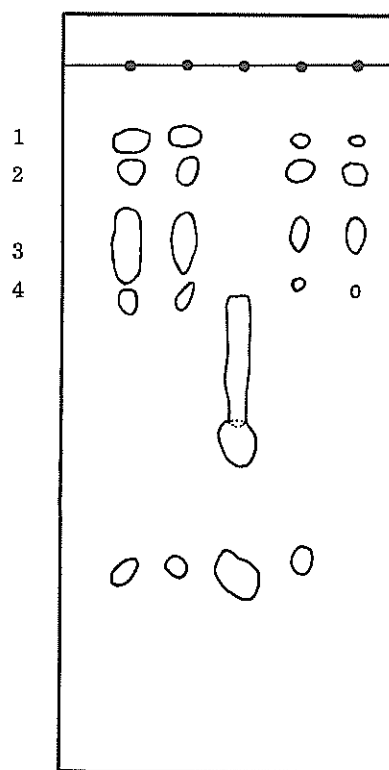


Fig. 29 Paper chromatogram showing anions in an acetone-water extract of quick clay from Lerum

to extract dispersing substances from clay and peat. This solvent therefore seems to be suitable. In the same way methanol and benzene-ethanol extract dispersing substances.

The first attempt to extract dispersing agents from quick clays were made as follows. About 500 g of natural quick clay was cut into small pieces and treated with 1 l of 90% acetone-water. The extraction time was 24 hours. The solution was filtered and the filtrate evaporated to dryness at 40°C. The residue was dissolved in about 300 ml water. Only the part of the extract soluble in water was analysed. The solutions were treated in the ion exchange columns and the three eluates were chromatographed as described above.

Experiments were made on samples of quick clay from Lerum, Rosshyttan and Ellesbo. (These experiments were made before the importance of the ageing effects had been taken into consideration.) The quick clay obtained from Lerum gave the acids shown in Fig. 29. No well known acids were present as in the Morsta and Porla waters. Iron and also amino acids and carbohydrates were present. This indicates dispersing substances of the iron condensation types. Small-paper chromatograms showed the presence of chloride, sodium, calcium, magnesium and organic ions. The cation eluate gave a negative result for free amino acids in the quick clays (cf. amino acids in the testing part, Ch. 6.3.3). No free sugars or polyphenols could be detected in the non-ionic fraction.

The chromatogram of the acids from the Rosshyttan quick clay is seen in Fig. 30. Nor could any well known acids be detected in this case, but acids of the same type as in the Lerum quick clay were found. Iron is found at every level in the profile. In the contact zone peat-clay, an acid with the same  $R_F$ -value as lactic acid appeared. Amino acids and carbohydrates were also found in the anion eluate. Only traces of free amino acids were present in the cation eluate and only traces of sugars and polyphenols in the non-ionic eluate. The dispersing properties of all fractions obtained from the ion exchangers are shown in Table 4.

The chromatogram of the acids from the quick clays

from Ellesbo are shown in Fig. 31. Artesian water obtained at this site was also investigated and contained several organic acids with relatively low  $R_F$ -value (0-0.35). The acids show a strong tendency to form "tails", and no individual acids could be separated. Spraying with ammonium molybdate - tin (II) chloride indicated the presence of some form of phosphoric acid (see App. 4). Small-paper chromatograms indicate the presence of chloride and sulfate ions. Ninhydrine-spraying indicates the presence of amino acids in the anion eluate. As seen later in this report, this artesian water also contains fatty and resin acids. Apart from the inorganic ions, the water contains polycondensation products. Probably they are of another kind than those occurring in quick clay.

The chromatograms from the quick clays show very complicated acid mixtures in the profile from Ellesbo, somewhat simpler towards the bottom layers. As seen from the chromatograms, simple diffusion or infiltration from the artesian water into the overlying clay layers is apparently not present. It does not seem possible from the results so far obtained to draw parallels between the acids found and the sensitivity of the profile, cf. Fig. 32, page 48. In addition there was, on each level, an acid with  $R_F \approx 0.67$  (the same value as for lactic and for succinic acid). As for the Rosshyttan clay, the cation eluate contained no sugars and polyphenols in free form.

#### 7.2.5 Conclusion and Discussion of Test Results

When the investigation started, the remote sensing method had not been worked out and it was assumed that all quick clays and all substances found in the clay profiles were of a natural origin. Additional investigations during the last few years have been made to check whether the places investigated are subjected to impurities or not.

The peat bog at Morsta, situated in a fairly elevated place, and its water seem to be "clean" and unaffected by outlets.

There are no outlets at Rosshyttan either (difficult to check with respect to storm water). The railway track

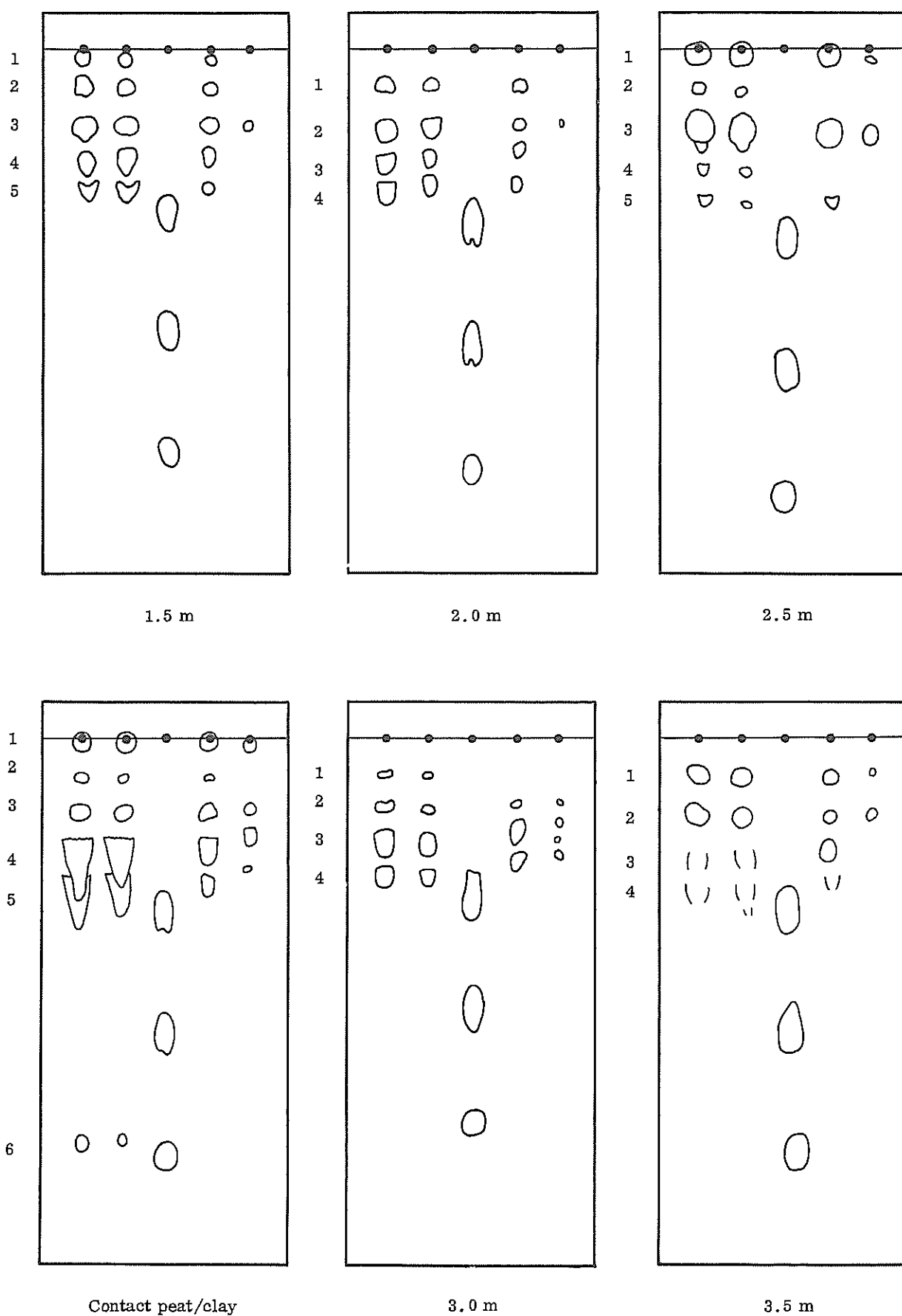
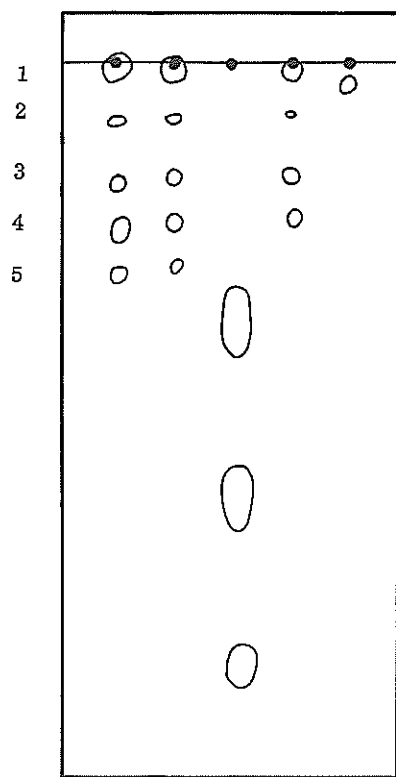
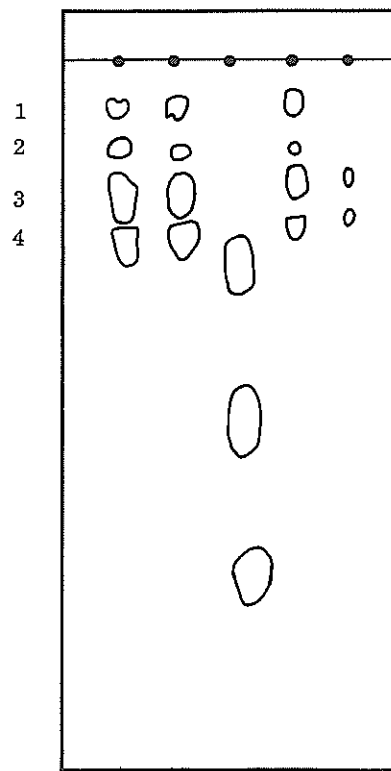


Fig. 30 Paper chromatograms showing anions in an acetone-water extract of quick clay from Rosshyttan



4.0 m



4.5 m

Fig. 30 Paper chromatograms showing anions in an acetone-water extract of quick clay from Rosshyttan (Continued)

Table 4 Dispersing properties of different eluates from Morsta, Lerum and Rosshyttan

Substance	Dispersing properties		
	Fraction real acids	Fraction amino acids etc.	Fraction phenols etc.
<u>Morsta and Lerum</u>			
Peat water from Morsta 2 months old	Will disperse obviously but not so strongly	Coagulates	Will disperse strongly
Peat water from Morsta (fresh)	Will disperse obviously but not so strongly	Coagulates	Will disperse strongly
Acetone extract from quick clay from Lerum	Will disperse strongly	Coagulates	Will disperse very weakly
<u>Rosshyttan</u>			
Peat 1.5 m	Weak	Very weak	Very good
Peat 2.0 m	Weak	Very weak	Very good
Peat 2.5 m	Good	Weak	Good
Contact 2.9 m	Rather good	Good	Good
Clay 3.0 m	Rather good	Very weak	Good
Clay 3.5 m	Rather weak	Weak	Good
Clay 4.0 m	Rather good	Weak	Good
Clay 4.5 m	Bad	Weak	Good

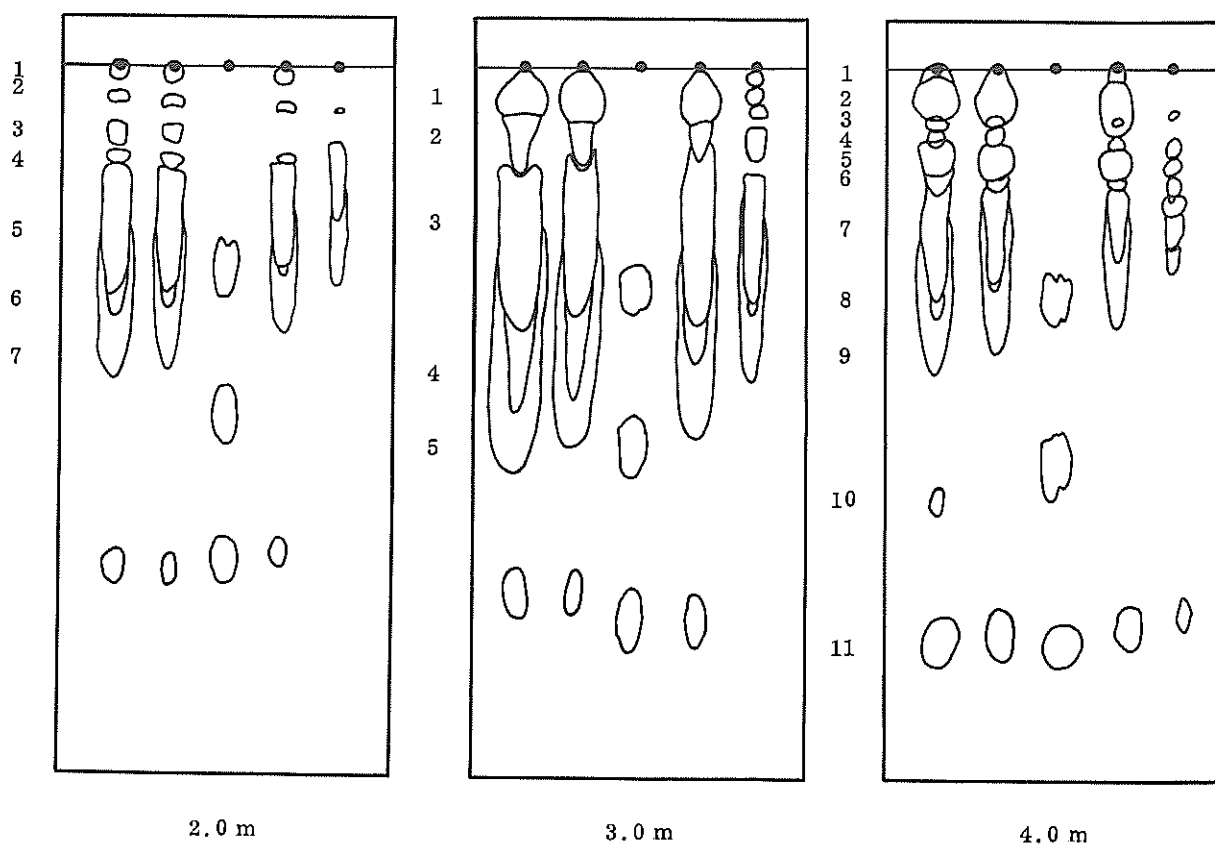


Fig. 31 Paper chromatograms showing anions in an acetone-water extract of quick clay from Ellesbo

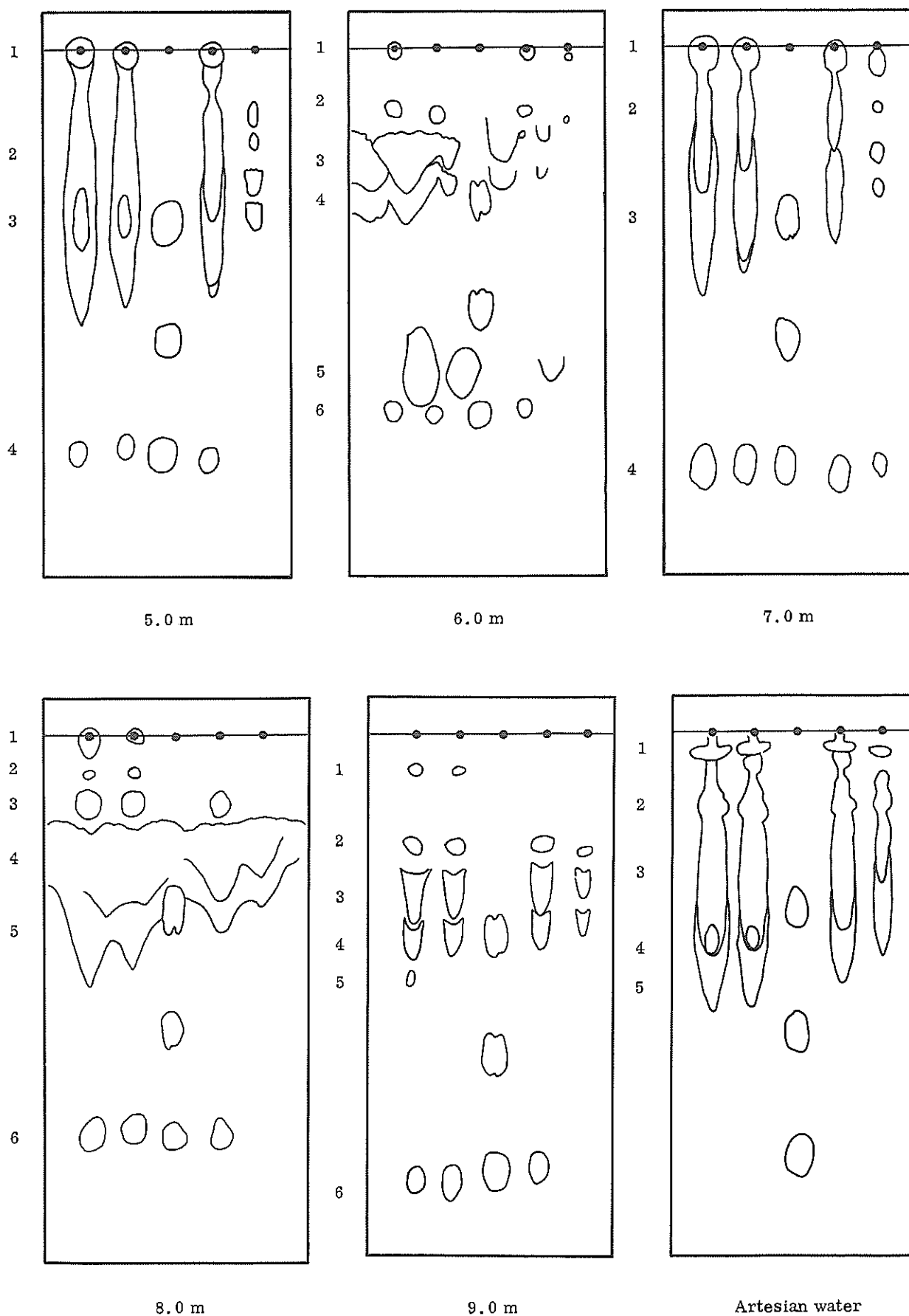


Fig. 31 Paper chromatograms showing anions in an acetone-water extract of quick clay from Ellesbo (Continued)

bed passing about 10 m from the test site is, however, filled with engine ashes which can spread impurities.

It is more difficult to express any opinions on the conditions at Ellesbo. The site is surrounded by a lot of houses situated at a higher level than the test site, and artesian water exists which can play a part in spreading impurities from existing sewage systems. The content of phosphoric acid in the clay indicates a possible occurrence of infiltration. Also the site at Lerum is surrounded by dwelling houses.

The water in the Porla Spring was considered by Berzelius (1833) to be a clean mineral water containing iron originating from strong "veins" from an adjacent peat bog. Recent remote sensing studies by the Author have shown that the area is rich in local ground water arteries in which impurities easily can spread. There was previously a health resort with a large population and today there is a village with a factory producing mineral water. This factory, situated about 100 m from the spring, has bottle washing machines operating continuously and using strong cleaning agents. Conditions for an infiltration are therefore very favourable and it seems difficult to regard this water as natural unaffected water. It has, however, the same properties as described by Berzelius, e.g., forming of ochre. All these facts about impurities were, however, not taken into consideration at the time of the main investigation in 1963.

The Porla water contained acids which are similar to the acids in the Morsta water. The similarity suggests that there is no definite difference between acids in the peat water and the crenic and apocrenic acids reported by Berzelius. They seem to be condensation products of amino acids, carbohydrates, polyphenols, etc., with iron. Further studies of the composition and structure of such acids are desirable but are outside the scope of this report.

The results from the present investigation do not indicate that Swedish peat waters contain simple substances of well known nature. Oxalic acid found by Alexandrova in Russian peat could not be detected in the Swedish water and clay samples examined. Possibly, Aleksandrova's addition of sulphuric acid can have given rise to a hydrolysis. The experiments

by the Author seem to confirm that, in agreement with Nykvist (1963), oxalic acid is instable. Hence, it does not contribute to the formation of quick clays in Sweden.

As seen from the small-paper chromatograms the acids obtained from the ion exchangers also contain hydrochloric and sulfuric acids. Most of the hydrochloric acid seems to come from the HCl used to eluate the acids. But also experiments made on untreated Morsta and Porla water indicate, as said before, the presence of chloride and sulfate ions and, in addition, there are organic acids of a probably complicated structure. Also cations such as  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  can be found in the acid eluate indicating very complex negative anions in the original state.

The presence of iron in the acid fraction can indicate that there are condensation products present of the type occurring in ferro chrome lignosulfonate dispersants. This will be discussed further in Ch. 7.4.1.

The acids with low  $R_F$ -values (0 - 0.40) found in the present investigation differ from those discovered by Ramaut (1955) with  $R_F$ -values 0.53 and 0.80. As will be seen later in this report, Swedish peat water yielded a similar acid when treated according to Ramaut's method (Ch. 7.3.3). Methods like Ramaut's with disintegration of metal precipitates with hydrogen sulphide cause a disintegration of complex products. For this reason, it is not certain that the acid found by Ramaut does exist in peat.

The acid with  $R_F \approx 0.70$  which is common in Swedish quick clay has the same  $R_F$ -value as lactic acid. It might be the second acid with  $R_F \approx 0.80$  found by Ramaut (this value refers to a slightly different solvent). Whether this acid is a derivative of succinic acid as stated by Ramaut is questionable. It can be lactic acid in accordance with Nykvist's results. Lactic acid formed by microbial action is a very important factor in soil weathering as stated by Kononova (1961). In the clay core from Rosshyttan, acids of the same type were found.

No simple dispersing substances of well defined character have been found in the investigation and the quick clay forming process cannot be explained from substances of simple chemical character. On the other

hand, dispersion agents in general, e.g. sodiumpyrophosphate, form high molecular micelles with water.

Reducing sugars have not been found in any of the complexes investigated. Non-reducing polysaccharides may occur and, theoretically, the dispersing process suggested by Emerson (1954) (Ch. 5.3.2.1) may take place. The analysis test for carbohydrates according to Molisch (1886) gave, however, only a weak indication in the present investigation.

Bloomfield (1954 and 1956) has suggested that polyphenols are active dispersing agents which are present in nature. Examinations of the Ellesbo and Rosshyttan extracts resulted in only a small amounts of such free substances. Instead, polyphenols seem to be associated with iron, forming dispersing agents of a complex composition (cf. U.S. Pat. 3 325 426 on Modified lignin compounds for drilling muds). Thus, well defined simple dispersing agents of the water soluble type do not exist in nature. Instead, the active agents are polycondensation products. The complex and unstable nature of the dispersing agent is also supported by the ageing phenomenon in clays and similar soils. Ageing effects occur in e.g. such crenic acid which was found already by Berzelius (1833). Such effects can also be seen in the fatty acid group as will be shown later in this report.

### 7.3 Isolation of Dispersing Agents by Different Methods

Many methods are described in the literature on isolating organic substances or their decomposition products from peat and other soils. Some of them were deemed to be suitable and therefore tried in the present investigation.

#### 7.3.1 Modified Isolation Method according to Michaels

Experiments on isolating dispersing agents from quick clays from Rosshyttan were made by means of the method described by Michaels (1958). Michaels used 6N sulphuric acid to remove the adsorbed substances from the clay. When dealing with organic dispersants

it is impossible to use this acid because by the evaporation process one obtains concentrated acid which transforms all organic substances to carbon. Formic acid was chosen because it is a relatively strong and volatile acid (and is a part of the chromatography solvent).

About 500 g of natural-moist clay (water content  $\approx 70\%$  of dry weight) was suspended in about 1000 ml of formic acid (98-99% Merck). The mixture was allowed to react for about 24 hours and the solution was filtered off and evaporated in vacuo at  $40^{\circ}\text{C}$ . The residue was dissolved in about 500 ml of water. A small part of the solution was examined directly by paper chromatography using different solvents. The remainder was treated in the ion exchangers as described previously (Ch. 7.2.1). The different eluates were analysed by means of paper chromatography. Some comparative chromatograms of possible disturbing substances were also made.

The chromatogram for the evaporation residue from the untreated formic acid solution, which was sprayed with the reagent for phosphoric acid (Waldi, 1955), indicated the presence of some type of a probably organic phosphoric acid. A test with ammonium molybdate, benzidin-sodium acetate (Vogel, 1945) showed the presence of soluble forms of silicic acid. A Chromatogram for polyphenols in butanol-acetic acid-water developed with  $\text{FeCl}_3 - \text{K}_3\text{Fe}(\text{CN})_6$  is shown in Fig. 33. The chromatogram shows the presence of a very complex mixture. Spraying with KSCN indicated that iron was also present in the long spots.

The eluate from the cation exchanger resin showed only traces of amino acids and the presence of simple sugars could not be detected in the neutral eluate. Only small amounts of polyphenols were found. The acid eluate from the anion exchanger gave 5 to 6 spots as seen in Fig. 34. When sprayed with rhodanide, two spots became visible indicating negative iron complex in the original solution. The comparison chromatogram for iron(III)chloride is shown in Fig. 35.

A small amount of eluate from the cation exchanger was dried and ignited. Thereafter, the water soluble salts were leached with a small amount of water and examined with the small-paper method. Sodium, calcium and magnesium ions could be seen in the chromatogram.



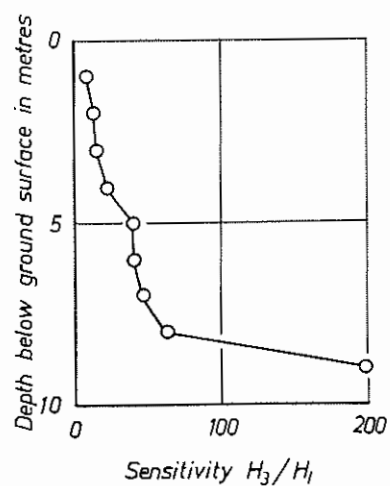


Fig. 32 Sensitivity curve of a clay profile from Ellesbo

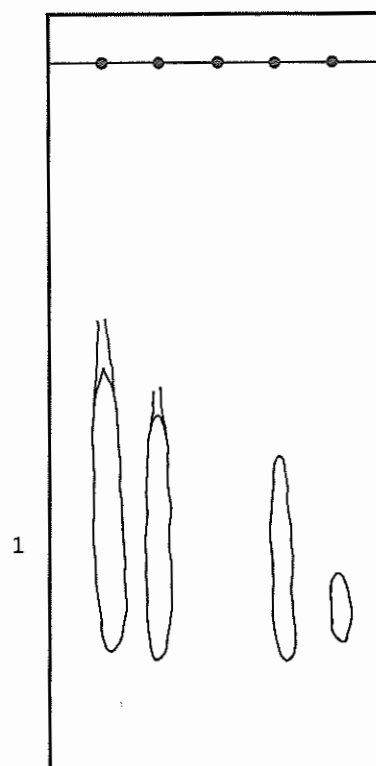


Fig. 33 Paper chromatogram of polyphenols in raw extract according to Michaels from Rosshyttan clay

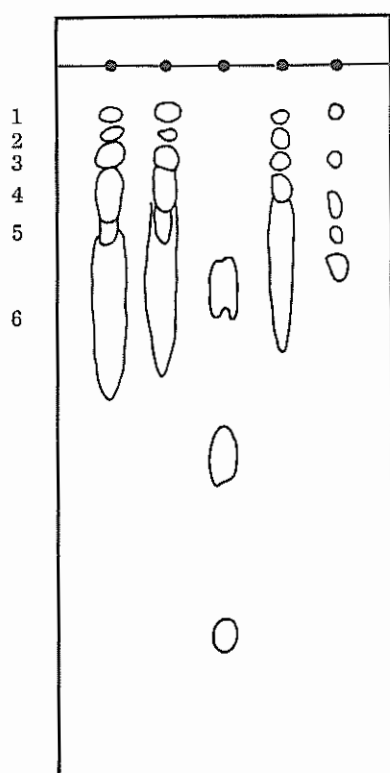


Fig. 34 Paper chromatogram of anion eluate of extract according to Michaels from Rosshyttan clay

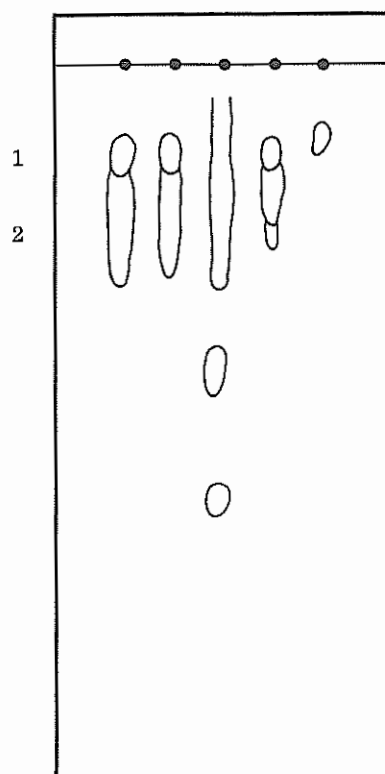


Fig. 35 Paper chromatogram of iron(III)chloride, 10% water solution

### 7.3.2 Attempts to Isolate Picolin-Carbonic Acid and Dihydroxystearic Acid from Peat

Picolin-carbonic acid and dihydroxystearic acid were isolated from Hawaiian soil by Schreiner & Shorey (1908a). Their method was repeated on peat from Rosshyttan which was allowed to react for 24 hours with 2% Na OH. The brown solution was filtered off. A slight excess of nitric acid was added to the clear alkaline solution. The acid filtrate was then neutralized ( $\text{pH} \approx 7$ ) by addition of sodiumhydroxide and the resulting new precipitate was removed. Silver nitrate was added to the solution and the new precipitate filtered off and washed. While still moist it was suspended in water, and hydrogen sulphide was passed through the suspension until the decomposition was complete. The silver sulphide was then removed and the filtrate evaporated. It was not possible to obtain any crystals of picolin carbonic acid as Schreiner and Shorey did. Only a brown amorphous mass was formed. This was examined chromatographically for the presence of acids and polyphenols. It was also tested for its dispersing properties.

The chromatogram of the acids in the water soluble part is shown in Fig. 36. Only one acid ( $R_F \approx 0.45$ ) was found. The mixture also contained polyphenols. A chromatogram, Fig. 37, shows the presence of several polyphenols which are probably of a complicated nature. A dispersing experiment showed that the mixture was a good dispersant.

In order to isolate dihydroxystearic acid the original alkaline solution was slightly acidified with acetic acid. After separating the humus precipitate, the extract was shaken out with ether which was allowed to evaporate on a small quantity of water. No crystals floating on the water were formed as Schreiner and Shorey had obtained. The water solution was then evaporated. The residue was analysed chromatographically and its dispersing properties examined.

As in the case of picolin carbonic acid, the evaporation residue was a brown-red amorphous mass. It had very good dispersing properties. When the mass was chromatographed, an acid with  $R_F \approx 0.70$  appeared (the same  $R_F$ -value as lactic acid). This fraction also

contained phenolic substances but in relatively small amounts.

The methods used are somewhat primitive, but are interesting because Schreiner and Shorey had succeeded in obtaining pure, definable chemical substances in this way. The isolation of substances of this kind will be discussed further in connection with peat and clay bitumens (Ch. 7.3.4 and 7.3.5).

### 7.3.3 Isolation of Acids from Peat according to Ramaut's First Method

Ramaut (1955) believed that peat contains substances which are acids with a definite composition which can be analyzed and tried to isolate them. If these anions are dispersing agents then this should offer a chance of identifying quick clay forming substances.

Peat from Rosshyttan was treated by 1% NaOH. Thereafter the suspension was filtered and the filtrate made slightly acidic by acetic acid. A solution of lead acetate was added and the new precipitate treated with hydrogen sulphide, as described above (Ch.7.3.2). A brown-yellow acid substance was obtained which was examined chromatographically and tested for dispersing properties.

The chromatogram of the acids prepared is shown in Fig. 38. Two acids appeared, one with an  $R_F$ -value of about 0.48 and the other of about 0.66. The mixture had strong dispersing properties. When purified according to the scheme shown in Table 5, substances with strong dispersing properties were found in the ethanol insoluble part of extract A (cf. Table 6). A chromatogram in 2% HAc sprayed for polyphenols is seen in Fig. 39. Several substances can be detected. The corresponding chromatogram of the ethanol soluble part is given in Fig. 40.

Also in this case dispersing substances appeared but it was not possible to identify any of them.

### 7.3.4 Isolation of Bitumen by Sundgrén's Method

Acids in peat, suspected to act as active dispersing

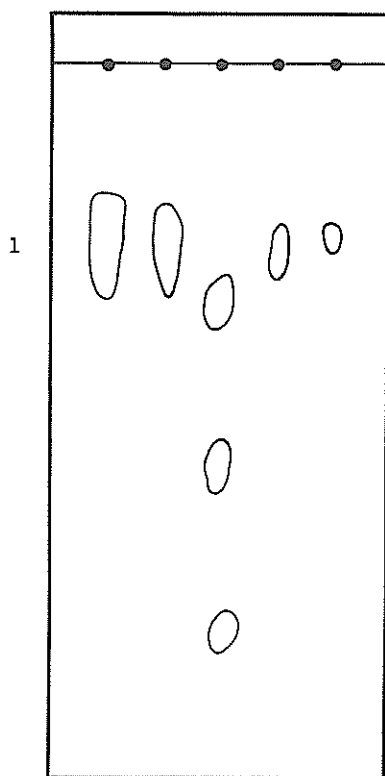


Fig. 36 Paper chromatogram of "picolin carbonic acid" isolated from Rosshyttan peat according to Schreiner & Shorey (water soluble acids)

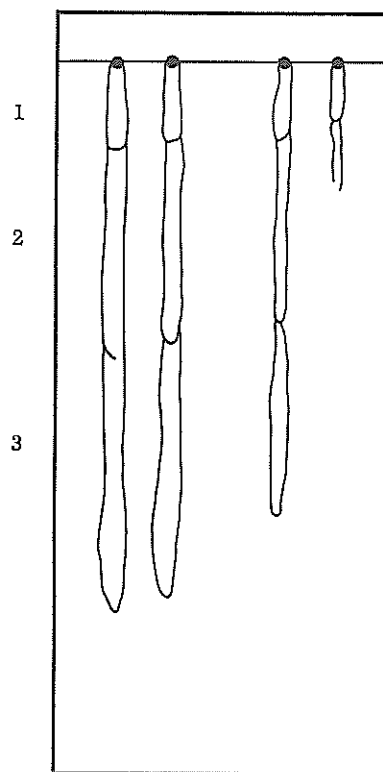


Fig. 37 Paper chromatogram of "picolin carbonic acid" isolated from Rosshyttan peat according to Schreiner & Shorey (water soluble polyphenols)

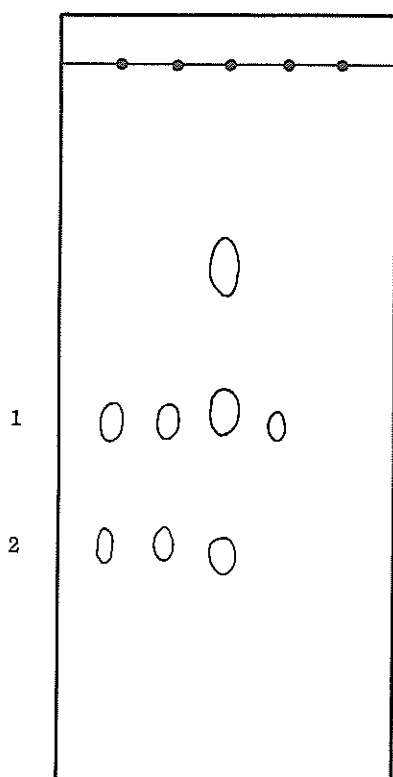


Fig. 38 Paper chromatogram of acids isolated from Rosshyttan peat according to Ramaut

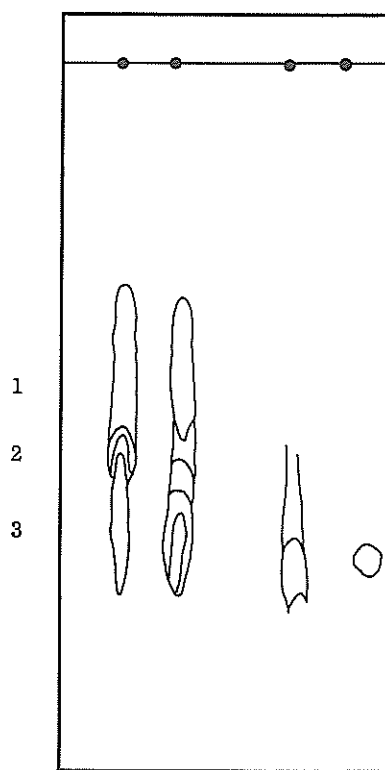


Fig. 39 Paper chromatogram of polyphenols isolated from Rosshyttan peat according to Ramaut. Extract A, unsoluble residue

Table 5 Purification scheme according to Ramaut (1955). Chromatograms 1-4 in the table refer to Ramaut's paper

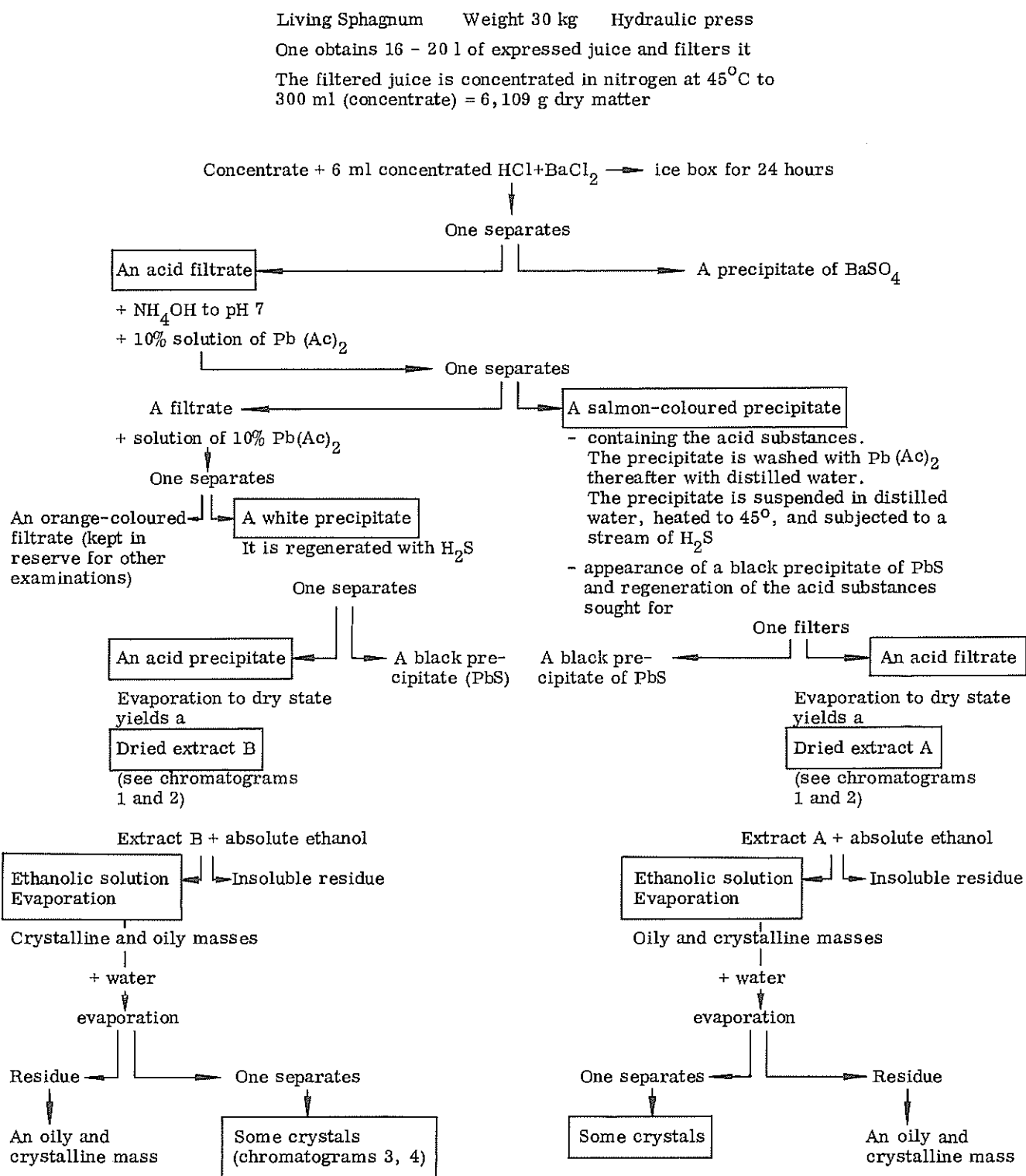


Table 6 Dispersing properties of different substances isolated in accordance with Ramaut's method

Substance	Dispersing properties
Acid prepared according to Ramaut by lead precipitation and treating with $H_2S$	Good
Extract A (cf. Table 5)	Good
Residue insoluble in ethanol	Very good
Substance soluble in ethanol	Good
Evaporation residue from peat water from Rosshyttan	Good

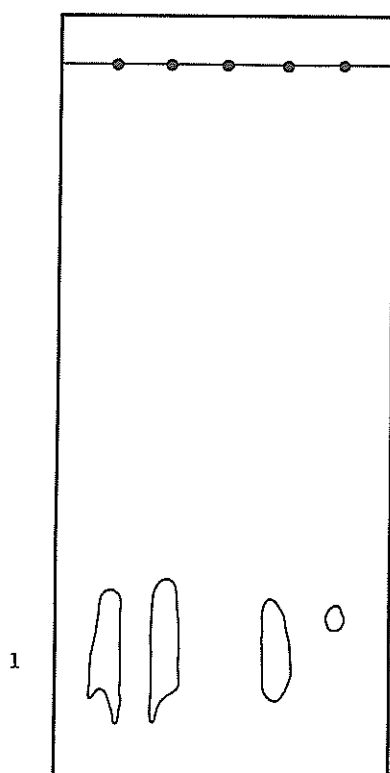


Fig. 40 Paper chromatogram of polyphenols isolated from Rosshyttan peat according to Ramaut. Extract A, soluble residue

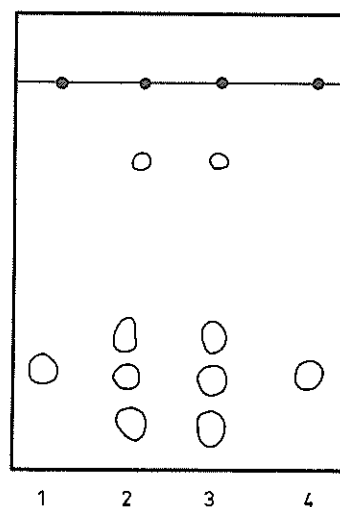


Fig. 41 Thin layer chromatogram of methylesters from Rosshyttan peat and quick clay isolated according to Sundgrén.  
1. Palmitic acid  
2. Peat from Rosshyttan  
3. Clay from Rosshyttan  
4. Palmitic acid

agents, have been isolated and studied according to a method used by Sundgrén & Rauhala (1965).

Experiments were made on peat from Rosshyttan, quick clays from Rosshyttan, Vesten and Ellesbo, and hymatomelanic acid from peat from Rosshyttan.

The peat and clay were carefully dried and pulverized and were then extracted for four hours with a mixture of benzene-ethanol (9:1) in a Soxhlet apparatus. The brown solution of bitumen was evaporated to dryness in vacuo. The evaporation residue was dissolved in boiling 95% ethanol and the filtered solution cooled to  $-20^{\circ}\text{C}$ . A brown-yellow precipitate of wax was formed. The wax was separated from the resin solution by means of a centrifuge and saponified for a period of 4 hours in 0.5*N* alcoholic KOH solution. Some water was then added and the unsaponified substances were extracted with petrol ether. The soaps were then precipitated by means of a 2% water solution of  $\text{CaCl}_2$  and the lime soaps filtered off and after drying, methylated by means of methanol-sulfuric acid (95:5) for a period of 4 hours. The methylesters were collected in carbon tetrachloride and separated from the methanol solution. The solvent was evaporated and the resulting ester dissolved in a small amount of chloroform.

These methylesters were then examined by means of thin-layer chromatography.

In the dispersing experiments the saponification was made with alcoholic NaOH and the resulting soaps examined for dispersing properties.

Both the peat and hymatomelanic acid and the quick clays examined contained substances soluble in benzene ethanol. The saponified peat bitumen showed dispersing properties as can be seen in Fig. 19. Both the bitumen from the peat and from the quick clays could be split up in a resin part and in a wax part. The results of the thin-layer chromatograms of methylesters from waxes of peat and quick clay are reported in Fig. 41. The similarity of the chromatograms of the waxes is remarkable. One of the spots in each chromatogram has the same  $R_F$ -value as that of higher fatty acids. (All methylesters of the higher fatty acids migrate to the same spot in the solvent system used.) This indicates that fatty acids or soaps may be one group of active

dispersing agents in the quick clay system. The methylesters from hymatomelanic acid were firstly dissolved in chloroform and chromatographed as in the case of peat bitumen. Thereafter, the solvent was evaporated and the fatty acid esters were extracted with petrol ether. They were purified twice by extraction with petrol ether. On the chromatograms obtained, not shown here, it was possible to distinguish between two fatty acid spots, one for saturated and one for unsaturated acids.

These methylesters showed ageing effects. After standing a few days the light-yellow substance gradually coloured and no fatty acid spots could be detected in the chromatograms. Similar results of ageing have been reported by Sundgrén & Rauhala (1952).

The amount of extractable bitumen in the Vesten quick clay was about 0.1% of the dry clay.

The Sundgrén isolation method gave dispersing agents which it was possible to identify thereby giving some interesting aspects on the quick clay problem.

### 7.3.5 Isolation of Bitumen by Rakowski and Edelstein's Method

A modified isolation method developed by Rakowski & Edelstein (1932) was also used. Moist peat was employed to avoid alteration of the acids during the drying process. The material was treated with benzene-ethanol (1:1) for 24 hours. The solution was then evaporated and the resin part extracted from the evaporate with methanol-acetone (1/2% acetone). The waxy part was then treated by Sundgrén's method. The resin solution containing acids was evaporated and tested for its dispersing properties and chromatographed. The water-insoluble part was also examined for its dispersing properties. It was dissolved in a few millilitres of methanol-acetone (1/2% acetone) and chromatographed.

The solution obtained by cold benzene-ethanol gave bromophenol blue a yellow colour. Acid substances from peat thus have been extracted by the solvent. The waxy part behaved like a normal peat wax and contained, among other things, fatty acids. The resin

part was most interesting in this case. It had typical acidic properties and contained a water soluble acid part. A chromatogram of the water soluble acids in this resin is shown in Fig. 42. When the acid was untreated, only one acid with  $R_F \approx 0.01$  was obtained, but when the solution was treated in the ion exchangers, acids of the same type as obtained in peat water and in quick clays appeared. Both iron and amino acids could be detected.

The resin also contained a part which was difficult to dissolve in water but which was soluble in methanol. This solution had acidic properties. It was possible to chromatograph this solution in butanol-formic acid-water and the results can be seen in Fig. 43. Also in this case acids with low  $R_F$ -value appeared.

The experiments gave the general result that substances with dispersing properties could be isolated. Acids from the peat had accumulated in the resin part. At this stage it has not been possible to identify these acids.

### 7.3.6 Isolation of Acids from Peat by Methanol

An experiment was made to extract acid substances from the peat by treating it with pure methanol (99%) for 24 hours. The solution was filtered and evaporated and the residue tested for its dispersing properties. It was then dissolved in water, and the water-soluble part evaporated and tested for dispersing properties. The water-insoluble part was also tested after saponification.

The acid substances extracted from peat with methanol gave the chromatogram shown in Fig. 44. Only one spot with  $R_F \approx 0.01$  was obtained but when a small amount of hydrochloride acid was added, the molecules hydrolysed and gave acid spots of the well known character, with 3 to 4 spots. All these substances had dispersing properties.

### 7.3.7 Discussion

The isolation of dispersing agents according to the method proposed by Michaels (1958) showed the

presence of silicic acid in quick clay from Rosshyttan (Ch.7.3.1). According to Michaels, silicic acid is always present in a dispersed clay system as a reaction product. Kvyatkovskaya & Chernov (1961) also believed that in many cases dispersing effects are caused by silicic acid and that by reaction with e.g. oxalates, silicic acid should be formed causing a dispersing of the clay.

The polyphenol diagram from the Author's tests indicated the presence of complicated substances bound to iron. This may indicate dispersants of the iron chelate type. It is in accordance with the results obtained by Lewis (1960). He states that simple polyphenols are leached from leaves and litter and infiltrated into the ground. When such substances come into contact with alkaline soils containing iron hydrates, the simple polyphenols will polymerise and form high molecular compounds. This can be an anaerobic microbial process. Probably the cementing iron hydrate is affected by reactions of this type causing a change in, e.g., the rapidity properties of the clay. Thus, there is only a small chance of finding simple polyphenols in the alkaline quick clay.

In this connection the chromatographical examination by Lewis (1960) of rain water dripping from trees is of interest. The water contained polyphenols in an easily detectable amount.

In principle, the experiments with extracting dispersing agents with formic acid gave the same importance of iron in the colloid chemistry of quick clays as discussed in Ch. 7.2.5. Trivalent iron in the form of cations or as positively charged hydrosol is a strong coagulating (and cementing) agent for a dispersed, negatively charged colloid system. In contrary, organic anions containing iron are strong dispersing agents and like natural organic material, iron can have two quite different influences in the quick clay formation process.

Ramaut's first isolation method with lead acetate has been used by several researchers to isolate substances of different kinds from biological fluids. Rakowski & Edelstein (1932) used the lead-acetate method to precipitate resin acids from peat bitumen. Furthermore, Lewis (1960) isolated polyphenols from leaf extracts by the same method. (Berzelius used copper

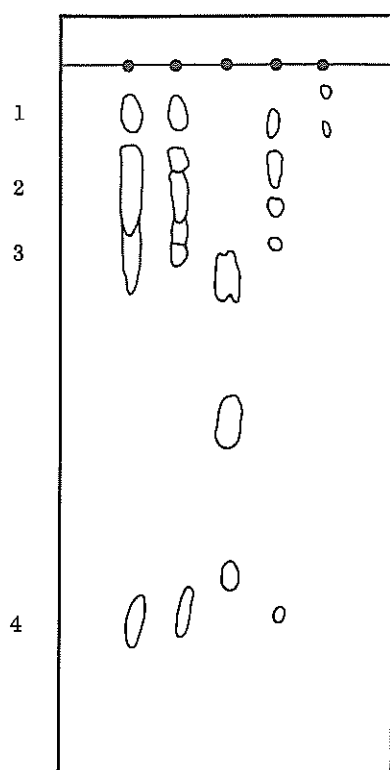


Fig. 42 Chromatogram of water-soluble resin acids in Rosshyttan peat

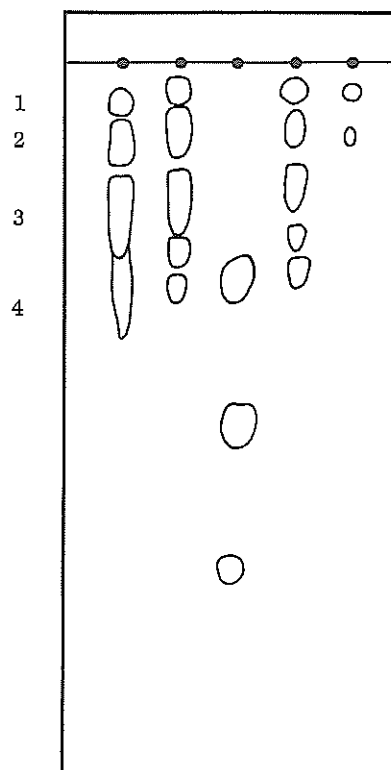


Fig. 43 Chromatogram of methanol-soluble resin acids in Rosshyttan peat

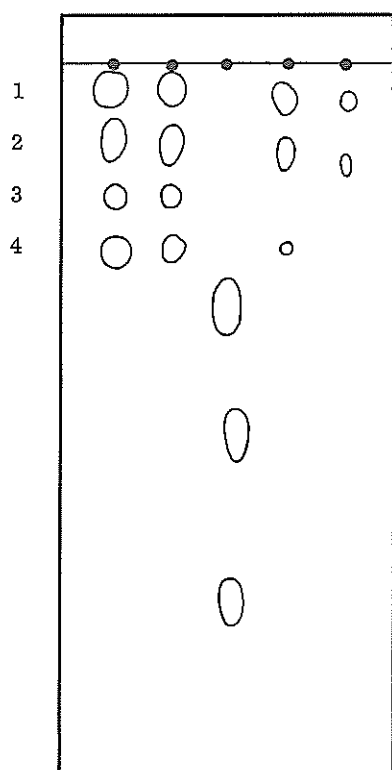


Fig. 44 Acids isolated from Rosshyttan peat by means of methanol

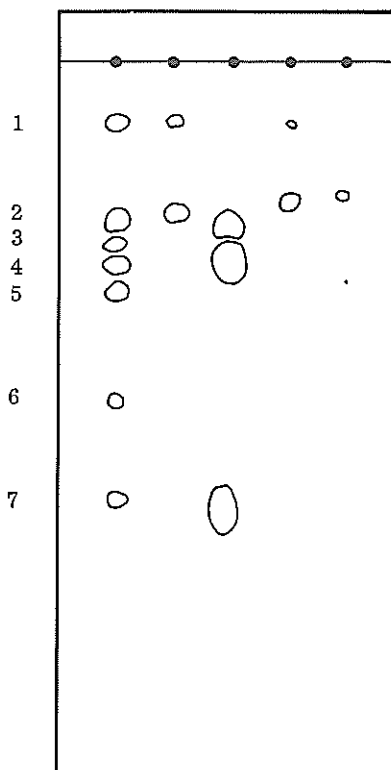


Fig. 45 Chromatogram of amino acids isolated from Porla water



acetate to precipitate crenic acid from ochre from Porla.) It is, therefore, uncertain whether the substances obtained really exist in the original extract or if they are formed during the chemical precipitation process.

Another fact in this connection should be noted. The peat water exhibited a very low reducing effect on  $\text{FeCl}_3 - \text{K}_3\text{Fe}(\text{CN})_6$ . After treatment with  $\text{PbAc}_2$  or  $\text{AgNO}_3$  and decomposing the precipitate with  $\text{H}_2\text{S}$ , the resulting product showed a strong polyphenol (reducing) reaction. The chromatogram also indicated the presence of a complicated mixture of polyphenols. These substances have probably been formed during the treatment of the precipitate with  $\text{H}_2\text{S}$  which is a strong reducing agent. This can indicate that one is dealing with quinoidic substances which are reduced to polyphenols. It is in accordance with results obtained by Mendez & Stevenson (1966) who obtained phenolic substances by a reductive cleavage of humic substances.

The substances obtained by the present Author are dispersing agents (Table 6) but it is likewise uncertain if these substances exist in nature.

The extracts obtained in the present investigation by the Schreiner and Shorey dihydroxy-stearic acid method may be real clay dispersants. The method includes no precipitation and reductive decomposition. Only dissolving with ether has been employed. The acid substance thus obtained is different from that obtained by metal precipitation. The acid with  $R_F \approx 0.70$ , which occurs in relatively small amounts, may be lactic acid (according to Nykvist) or it may be the homologue of succinic acid as found by Ramaut. The phenolic substances in this case seem to play a subordinate role, and the dispersing effect must originate from other types of substances. Fatty and probably oxy-fatty acids are present. Mixtures of this kind age in a few days and this ageing gives rise to experimental error.

Active dispersing agents are found in the bitumen part of the organic material containing fatty acids and resin acids. The presence of small amounts of fatty acids in quick clays obviously contribute to its high sensitivity. This is in accordance with the experimental results obtained by Quirk (1952) and Emerson (1954).

Emerson stated that it is not possible to obtain the deflocculation effect without the influence of some organic material which neutralizes the positive edges of the clay crystallites. The same fact has been mentioned by van Olphen (1965).

## 7.4 Further Examination of Natural Waters, Peat and Quick Clays

The preceding part of the present investigation gives an indication of different dispersing agents in the quick clay forming process. Dispersing agents are formed when simple substances such as sugars, urea, amino acids, phenols are transformed into condensation products by anaerobic microorganisms. These simple substances can be formed by decomposition of plant residues etc. in the clay, but in special geological formations (e.g. lee formations where an infiltration can easily occur) the substances can be supplied from septic tanks, dung hills, etc.

The addition and removal of substances from a clay is in principle a ground water problem and is treated in another paper (Söderblom, 1974). Experiences reported there from e.g. the slide at Jordbro indicate that infiltrated organic substances under favourable geological conditions can spread over relatively large areas in a short time.

As stated in Ch. 5.2.4 the crenic acid isolated from the Porla water showed ageing effects and was transformed into brown apocrenic acid. This process can be a basis for understanding the ageing effects of quick clays. Therefore, the experiments were started with some studies of Porla water.

### 7.4.1 Examination of Water from the Porla Spring

#### 7.4.1.1 Ionic Eluates

5 litres of water from the Porla Spring were allowed to pass through the ion exchangers. Two parallel tests were made.

The ion exchangers through which the original water

had passed were eluted, the cation exchangers with 1N  $\text{NH}_3$ , and of the anion exchangers one with 1N  $\text{HCl}$  and one with 1N  $\text{HCOOH}$ . The cation eluates were evaporated and examined for amino acids by paper chromatography in the solvent system butanol-acetic acid-water (4-1-5). The anions eluted were evaporated and examined for acids.

The analysis of amino acids in the eluate from the cation exchangers can be seen in Fig. 45. The Porla water contains a number of amino acids of which  $\alpha$ -alanine, leucine and glutamic acid are identified.

Fig. 46 shows the chromatogram obtained from the acids eluted from the anion exchanger with hydrochloric acid. The result is about the same as in Fig. 28. Two spots of iron can be detected with ultra violet light or  $\text{KSCN}$ , one of them corresponding to the Fe-spot from  $\text{FeCl}_3$  (Fig. 35).

The eluate with formic acid shows a quite different chromatogram than the hydrochloric eluate. No acids reacting with bromophenol blue were detected. The chromatogram gave no colour with  $\text{KSCN}$ . When hydrochloric acid was added to the eluate, it took on a yellow colour and thereafter gave a red colour with  $\text{KSCN}$ .

The results obtained indicate that there are complicated products which are adsorbed in the anion exchanger column. They are negatively charged complexes of iron indicating the formation in situ of substances of the ferro chrom lignosulfonate type. To get further information of the ligands of the eluate and to get rid of the iron, the following experiment was made.

A specially made hydrochloric eluate containing  $\text{Fe}^{3+}$ -ions, originating from the decomposition of the negatively charged iron complex, was shaken out with ethyl ether and the ether layer separated, evaporated and chromatographed. The same experiment was made with chloroform and with benzene.

The results with ether are shown in Fig. 47. In this case some faintly apparent acid spots with low  $R_F$ -value are seen, but above all a very strong spot from an acid with an  $R_F$ -value somewhat higher than that of lactic acid can be noted.

The chloroform extract has no visible acids but the benzene extract has acids of the tail-forming character (Fig. 48). This chromatogram shows no absorption spots of iron in UV. The acid tail shows a weak absorption but gives no colour with  $\text{KSCN}$ . It gives a weak reaction with the spray reagent for phosphoric acid.

A shaking out of the eluate with suitable organic solvents therefore seems to give the ligands bound to iron, and can give valuable information on the structure of the natural dispersing agents of humic basis.

#### 7.4.1.2 Non-Ionic Eluates

The non-ionic eluate, which had passed both the cation and anion exchangers, was evaporated to dryness and the residue dissolved in about 250 ml water. The solution was decomposed by means of hydrogen sulphide for about 3 hours. A black precipitate of iron(II)-sulphide was formed. It was filtered off and the filtrate was now an acid liquid, which contained the liberated ligands. The liquid was evaporated and part of the residue examined for acids by paper chromatography.

The rest of the residue was diluted to 100 ml water and was allowed to pass a regenerated cation exchanger (IR 120), in which part of the substance was adsorbed. The solution passing the ion exchanger was evaporated and was examined by paper chromatography for acids.

The  $\text{FeS}$ -precipitate on the filter paper was boiled with ethanol for 10 minutes, after which the liquid was filtered while hot and the filtrate cooled to  $-20^\circ\text{C}$ , giving a precipitate of wax.

The results of the complete treatment of the Porla water is summarized in Table 7.

The results from the chromatogram of the untreated acid substances originally bound to iron are shown in Fig. 49. These substances have hardly shown any migration in the solvent system used and seem therefore to be of a complicated nature. The chromatogram of the acids purified in the cation exchanger is shown in Fig. 50. It is possible to distinguish some acids. The chromatogram of the eluate purified in the anion exchanger is seen in Fig. 51. Very strong indications

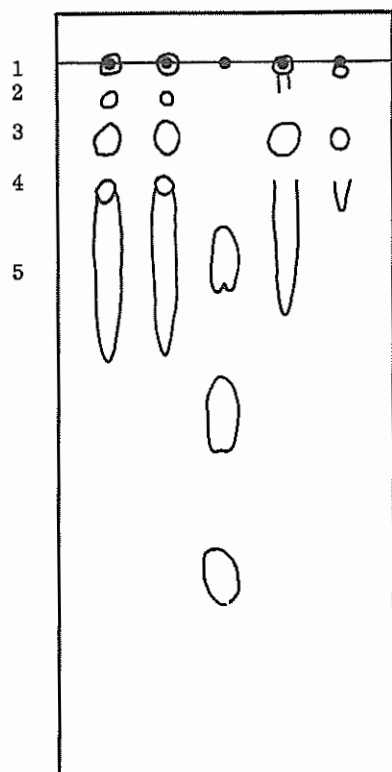


Fig. 46 Chromatogram of anion eluate by means of HCl from Porla water

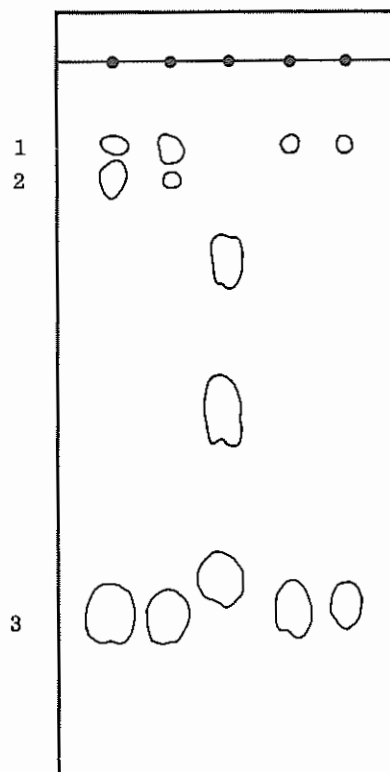


Fig. 47 Chromatogram of ether extract of anions containing iron from Porla water

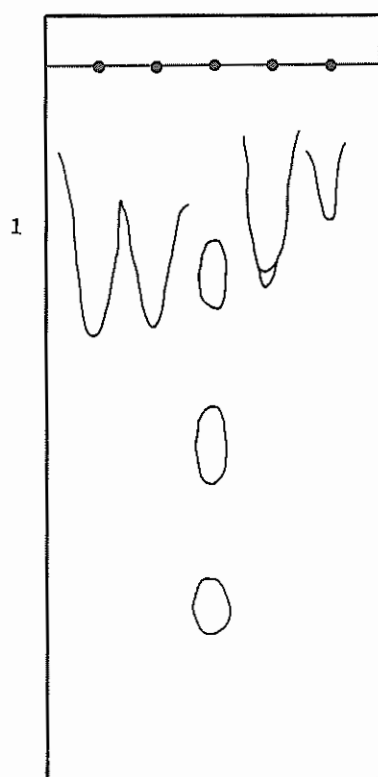


Fig. 48 Chromatogram of benzene extract of anions containing iron from Porla water

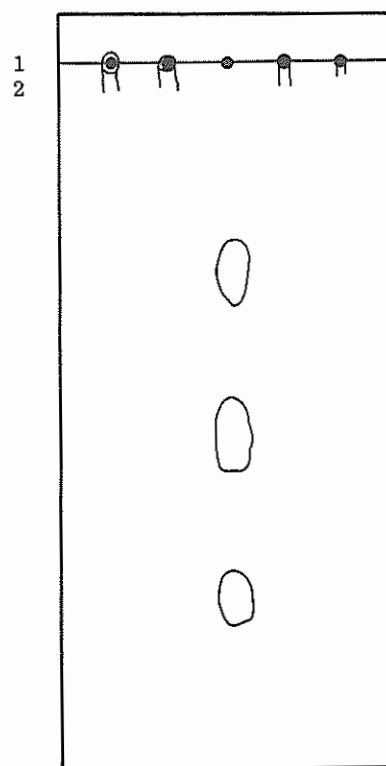
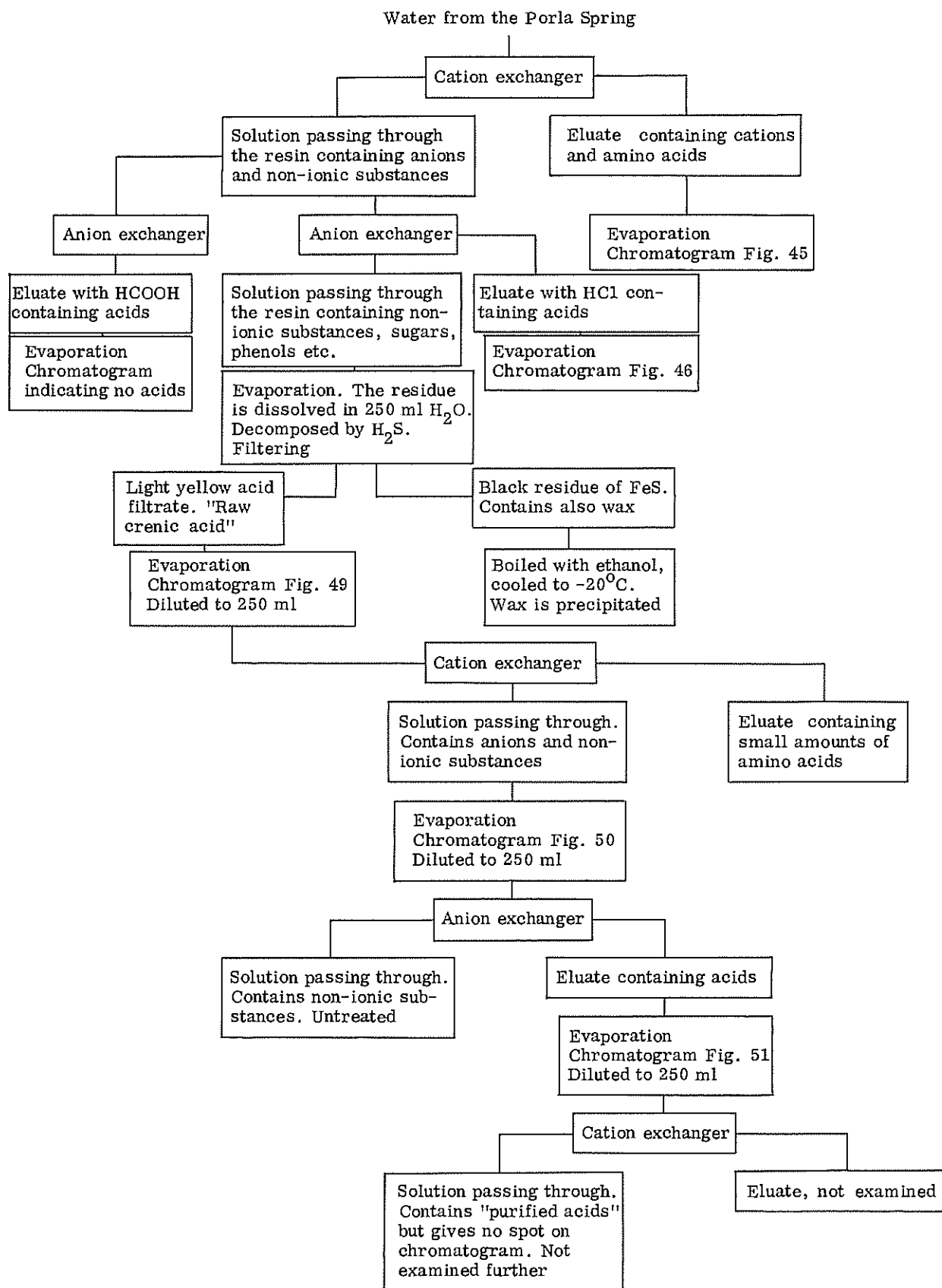


Fig. 49 Chromatogram of "raw crenic acid"

Table 7 Purification scheme of water from the Porla Spring



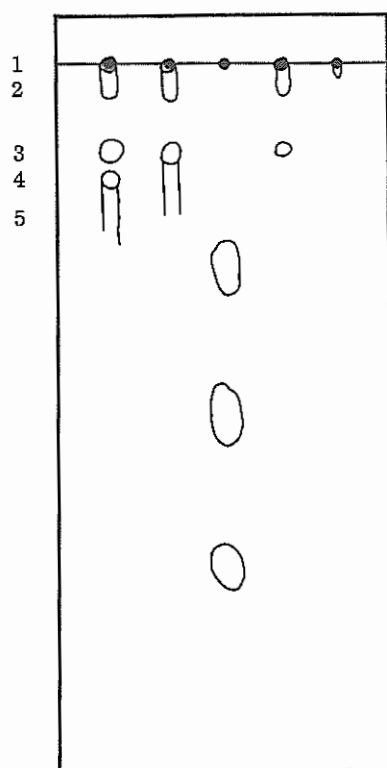


Fig. 50 Chromatogram of "raw crenic acid" purified in a cationic exchanger

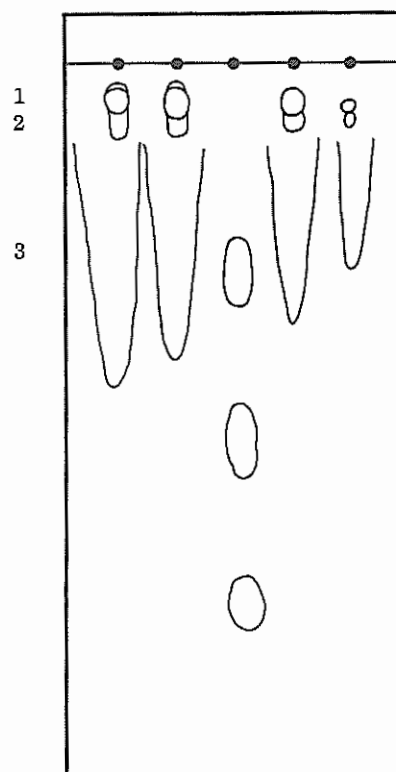


Fig. 51 Chromatogram of "raw crenic acid" purified in both a cation and an anion exchanger (eluted with HCl)

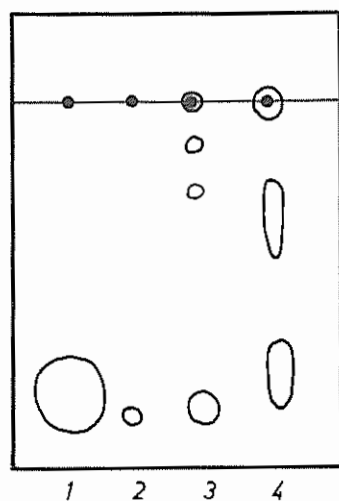


Fig. 52 Thin-layer chromatogram of methylesters of  
1. Palmitic acid  
2. Crenic acid  
3. Surface peat from Rosshyttan  
4. 12-hydroxy stearic acid, techn.

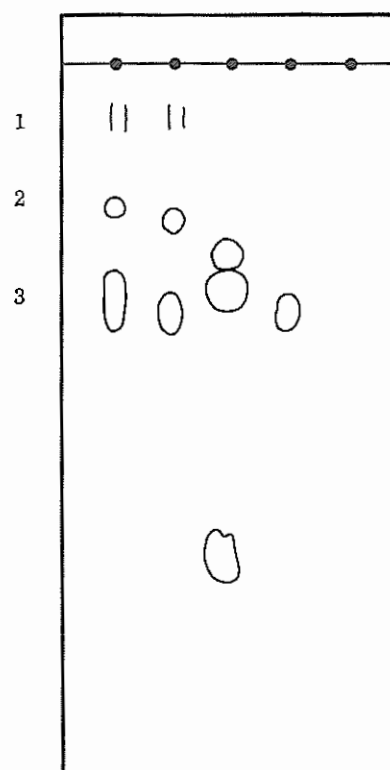


Fig. 53 Chromatogram of amino acids in peat water from Rosshyttan

of acids were obtained. In ultra violet light the unsprayed chromatogram showed two distinct absorbing spots. Sprayed with  $(\text{NH}_4)_2\text{S}$  they adopted a blue-black colour and sprayed with  $\text{KSCN}$  they appeared red. The spots therefore contained trivalent iron showing that the original  $\text{H}_2\text{S}$ -treatment was not enough to split off the iron complex. When the iron and other cationic substances were removed from this solution in a third cation resin, the solution showed only a very small amount of acids. In the eluate from this third cation exchanger, amino acids were present.

The hydrogen sulphide precipitate contained wax to an amount of 3.6 mg/l original water, about 8-10% of the total organic content of the water.

The results can be briefly summarized as follows. The non-ionic fraction of the Porla water contains anions which are complex-bound to Fe which can be freed by means of  $\text{H}_2\text{S}$ . These acids seem to form a complicated chelate with Fe. It has not been possible to purify them by means of ion exchangers, because they disappear if treated with a cation exchanger.

#### 7.4.1.3 Non-Ionic Eluate by Direct Saponification

As seen above, the non-ionic fraction contains wax. It is possible to free the acids by direct saponification and to analyse them. The dried material of about 0.4 g (from 5 l water) was boiled for four hours with 0.5n KOH and the saponified mass treated according to the same procedure as the saponified bitumen (Ch. 7.3.4). The lime soaps obtained were filtered off and esterified for four hours with methanol-sulphuric acid (95-5). The methylesters were analysed with thin-layer chromatography.

The filtrate from the lime soaps contained ions forming soluble calcium salts. They were purified in a cation exchanger and chromatographed.

The results of the thin-layer chromatographing of the methylesters are shown in Fig. 52. It indicates the presence of methylesters of fatty acids. In the case of chromatographing the non-lime precipitable acids, some weak spots of acids with low  $R_F$ -value were

obtained. When refining the acids in the anion exchanger resin, the chromatogram showed the same tendency as in the case of crenic acid (Fig. 51). Distinct spots of acids were obtained but they disappeared when the sample was purified in the cation exchanger.

In the eluate from the exchanger, some amino acids were observed in small amounts and one substance gave colour both with ninhydrine and with the spray reagent for phosphoric acid.

All the experiments with Porla water indicated the importance of iron complexes in the natural substances. In many cases these substances have strong dispersing properties, but as has been the case in earlier experiments, only the fatty acids could be identified.

In order to work with a material more closely related to the quick clay problem, the work was continued with water from Rosshyttan.

#### 7.4.2 Examination of Water from Rosshyttan

##### 7.4.2.1 By means of Ion Exchangers

Peat water from Rosshyttan was percolated through the ion exchangers as described before. The amino acids were eluted with 1n  $\text{NH}_3$ , and the acids in one experiment with 1n HCl, in another with 1n HCOOH and in a third with 1n ammonium carbamate  $\text{NH}_4\text{CO}_2\text{NH}_2$ . All extracts were evaporated and in the third case, the  $\text{NH}_4$ -ions were removed in a cation exchanger. The amino acids and the three sets of acids obtained from the anion exchangers were examined by means of paper chromatography. The amino acids are shown in Fig. 53. Somewhat fuzzy results were obtained.  $\alpha$ -alanine could possibly be observed.

The three anions eluted gave different results (Figs. 54-56). In the case of HCl, the anionic iron complex was split off and eluates containing iron were obtained. Since formic acid cannot split off this complex, only traces of acids were eluted (Fig. 55). Ammonium carbamate precipitated the iron in the ion exchanger mass and the acid ligands were eluted.

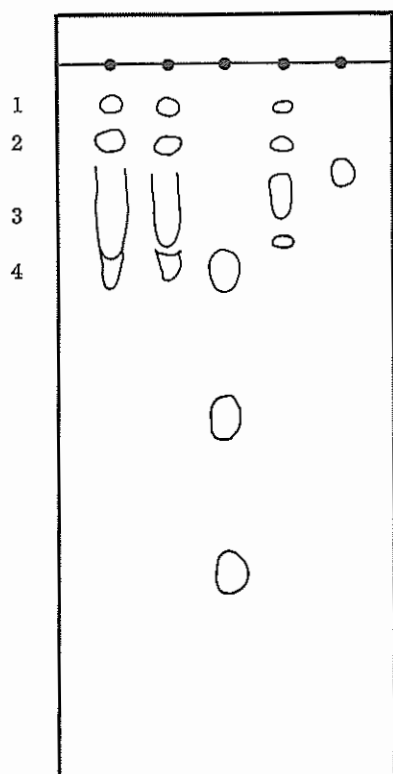


Fig. 54 Chromatogram of acids in peat water from Rosshyttan eluted with HCl

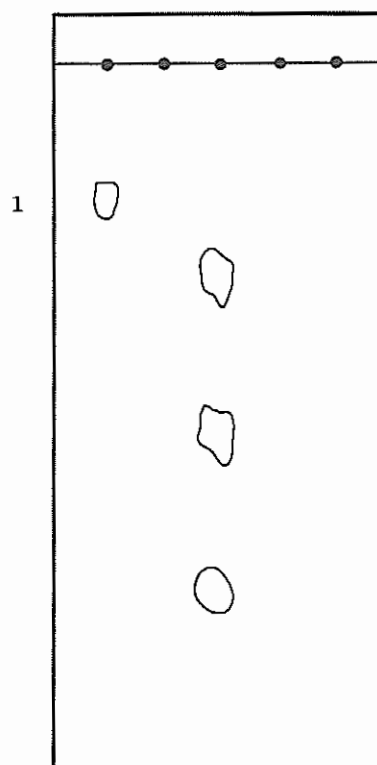


Fig. 55 Chromatogram of acids in peat water from Rosshyttan eluted with HCOOH

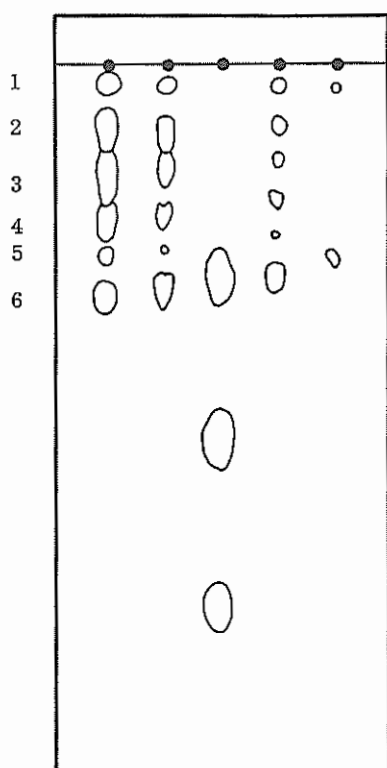


Fig. 56 Chromatogram of acids in peat water from Rosshyttan eluted with  $\text{NH}_4\text{CO}_2\text{NH}_2$  and purified in a cation exchanger

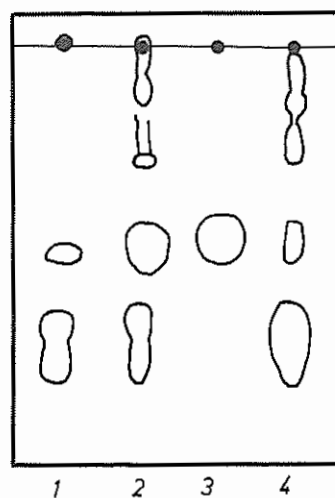


Fig. 57 Thin-layer chromatogram of  
1. HCl eluate from an anion exchanger containing acids from Rosshyttan peat water  
2. Foam from Morsta  
3. Palmitic acid  
4. Ochre from Porla

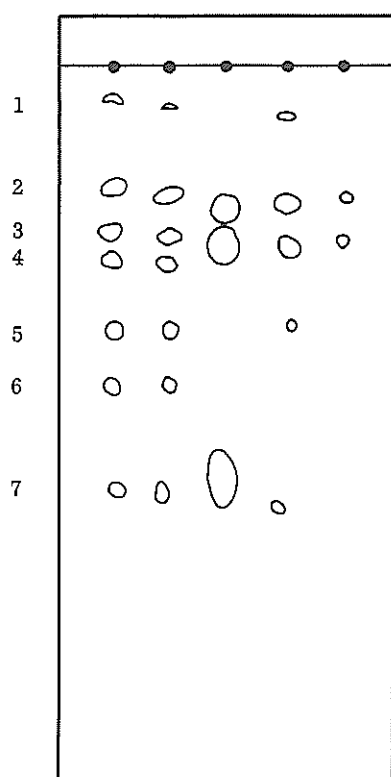


Fig. 58 Chromatogram of amino acids isolated from Rosshyttan peat water by means of active carbon

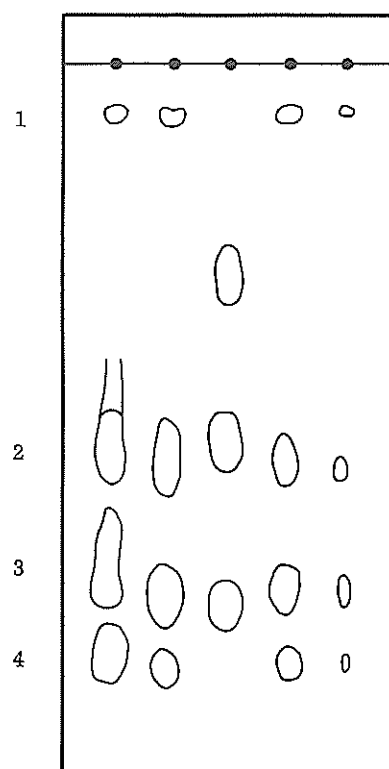


Fig. 59 Chromatogram of acids isolated from Rosshyttan peat water by means of active carbon

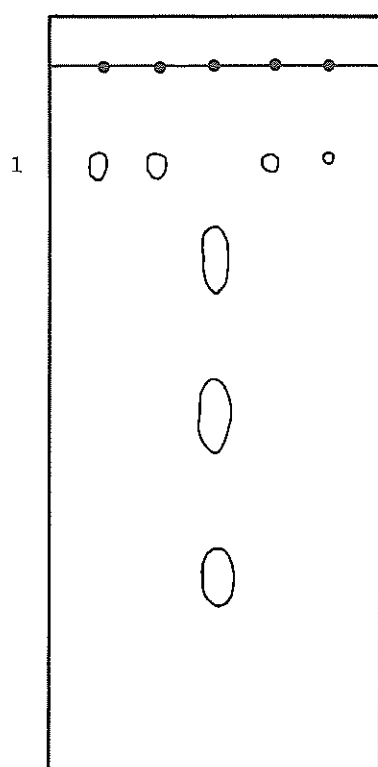


Fig. 60 Chromatogram of acids in ether eluate isolated from Rosshyttan peat water by means of active carbon

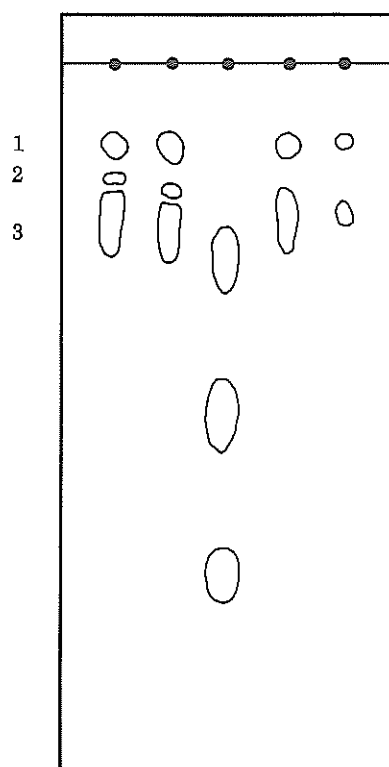


Fig. 61 Chromatogram of acids in ethanol eluate isolated from Rosshyttan peat water by means of active carbon



5 - 6 acids with a relatively low  $R_F$ -value were found (Fig. 56). The acid with the highest  $R_F$ -value gave a positive reaction with the spray for phosphoric acid. The acids eluted with carbamate can be purified in a cation exchanger without disappearing and seem to be real humus components.

The results clearly indicate that the dispersing properties of the Rosshyttan water originate from substances complexly bound by iron.

Experiments were made to examine the acids by means of thin-layer chromatography in different solvents but led to no results. Instead, experiments were made to produce the methylesters of the acids and to examine them with thin-layer chromatography.

#### 7.4.2.2 By means of Methylesters

The ion containing eluate with 1N HCl was evaporated and methylated with  $\text{CH}_3\text{OH} - \text{H}_2\text{SO}_4$  (Ch. 7.3.4) and the esters obtained were examined with thin-layer chromatography.

The eluate gave volatile yellow methylesters. The results of the thin-layer chromatography are shown in Fig. 57. A spot, apparently of fatty acid methyl-esters, and a spot with a higher  $R_F$ -value were noticed.

#### 7.4.2.3 By means of Active Carbon

Peat water from Rosshyttan was also studied according to the method used by Forsyth (1947).

3 litres of peat water were filtered through a column of active carbon. Most of the coloured substances were adsorbed. The almost colourless filtrate was allowed to pass through the ion exchangers. The eluates were examined by means of paper chromatography.

The adsorbed substances were eluted from the carbon in their proper turn by benzene-ethanol (9 - 1), diethyl ether, ethanol, acetone-water (9 - 1) and 0.5N NaOH. All eluations except the last mentioned were carried

out in a Soxhlet apparatus. The benzene-ethanol eluate was evaporated and separated into a wax part and a resin part (Ch. 7.3.4).

The ether, ethanol and acetone eluates showed acid reactions and all of them were chromatographed for acids. The acetone eluate was also chromatographed for polyphenols.

The result of the chromatographing of the amino acids in the cation exchanger eluate is shown in Fig. 58. At last 7 amino acids are visible, among others  $\alpha$ -alanine, leucine and glutamic acid. The acids eluted from the anion exchanger resin are shown in Fig. 59. Three acids with relatively high  $R_F$ -values appear as very strong spots. In the benzene-ethanol eluate was present (8 mg/l). The amount was too small to be saponified and chromatographed.

The chromatograms from the ether, ethanol, acetone and water eluates are shown in Figs. 60-63. The ether eluate contains one acid with a relatively low  $R_F$ -value.

The ethanol eluate showed two acids with a low  $R_F$ -value and the acetone eluate one acid with an  $R_F$ -value somewhat lower than that of tartaric acid. The acetone eluate also contained polyphenols. A chromatogram of polyphenols in 2% HAc is shown in Fig. 64. Several polyphenols can be observed.

The water eluate contained only traces of amino acids, but several real acids were observed (Fig. 63). Especially remarkable is the acid with the highest  $R_F$ -value. The spray for phosphoric acid gave a positive reaction. It has, however, a somewhat lower  $R_F$ -value than orthophosphoric acid ( $R_F \approx 0.33$ ).

In the experiment described in Ch. 7.4.2.1 only one amino acid could be identified from the ion exchanger, but in the present examination with active carbon, 7 distinct spots of amino acids were obtained. This shows that disturbing reactions occur in the ion-exchanger experiments if the substances are not purified before the treatment. In such a case well defined substances will be lost. Examination of waters of this kind should preferably be carried out by means of such methods as those involving the use of active carbon.

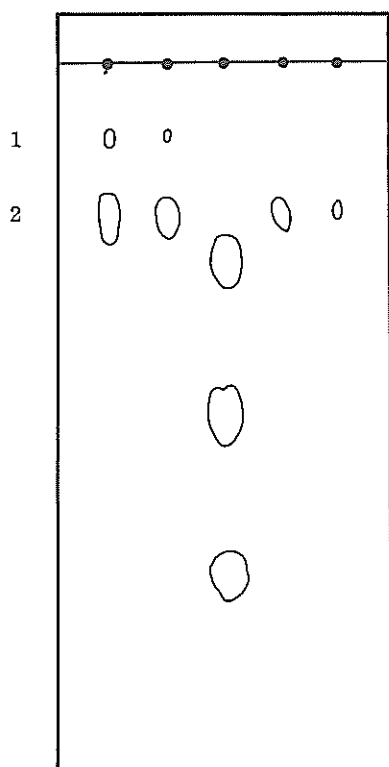


Fig. 62 Chromatogram of acids in acetone eluate isolated from Rosshyttan peat water by means of active carbon

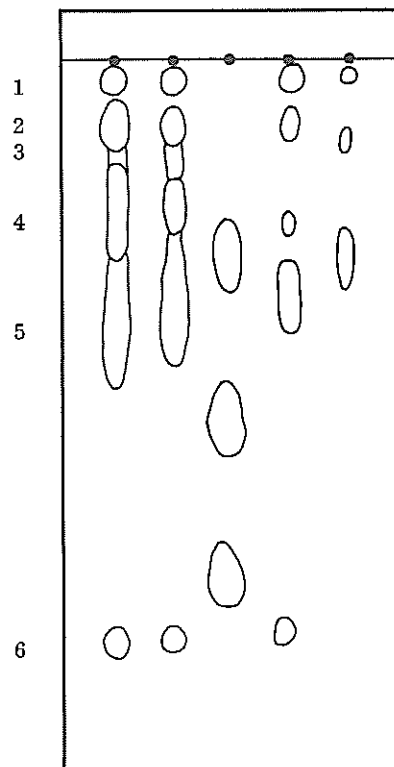


Fig. 63 Chromatogram of acids in water eluate isolated from Rosshyttan peat water by means of active carbon

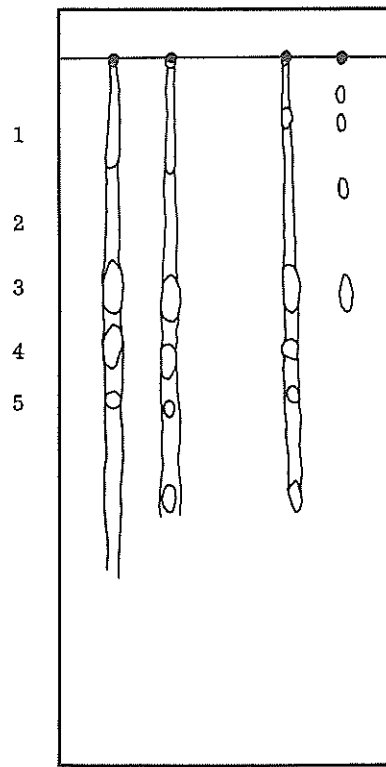


Fig. 64 Chromatogram of polyphenols in acetone eluate isolated from Rosshyttan peat water by means of active carbon

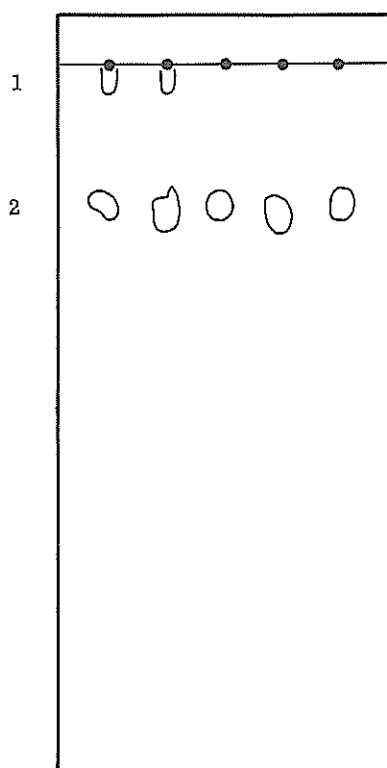


Fig. 65 Chromatogram of volatile acids from Rosshyttan peat water

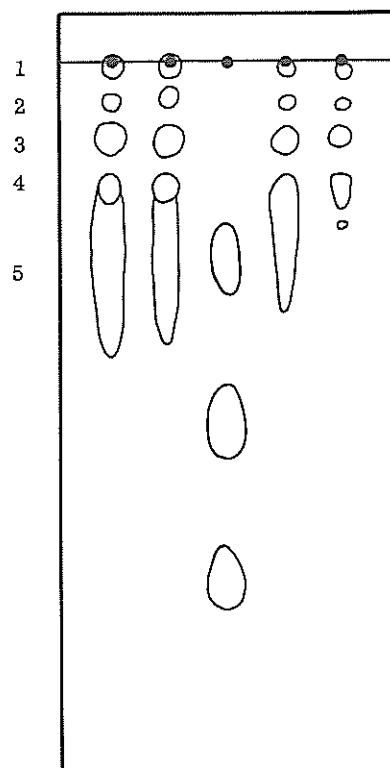


Fig. 66 Acids from Morsta collected in an anion exchanger in situ

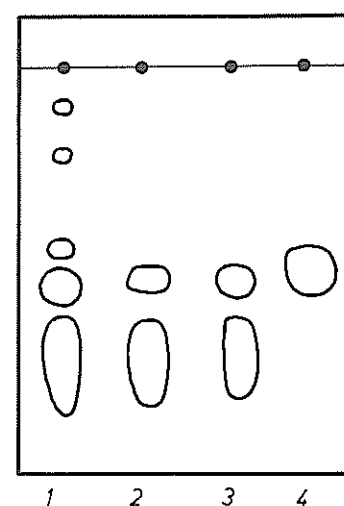


Fig. 67 Thin layer chromatogram of methylesters of  
1. Peat bitumen from Rosshyttan  
2. Artesian water from Munkedal  
3. Ochre from Porla  
4. Palmitic acid

### 7.4.3 Examination of Foam from Morsta

200 g of foam from peat water flowing in open ditches in Morsta was dried. In this case it was impossible to use the evaporator because the liquid showed strong tendencies to splash over. Instead, it was dried in a water bath. The dried grey mass was saponified, the methylesters were produced and then examined by thin-layer chromatography.

The chromatogram of the methylesters is shown in Fig. 57. A very strong spot of fatty esters can be noticed as can some other spots.

It is obvious that the foam contains fatty acids, indicating microbial processes. As shown in the testing part (Ch. 6), substances of this kind can cause a dispersing effect.

### 7.4.4 Examination of Volatile Acids in Water from Rosshyttan

According to Ramaut (1955), peat contains an acid with an unpleasant smell, which implies that the acid must be volatile and can therefore be distilled from the water. In order to study the conditions in Sweden the following experiments were made.

5 l of the water was evaporated and the distillate was made slightly ammoniacal. The liquid was evaporated again. About 5 mg of a light-yellow salt with slight dispersing properties was obtained. It was then examined with paper chromatography in the ethanol-ammonia (99-1) system and also by means of infrared spectra.

The chromatography of the volatile acids in the Rosshyttan water is shown in Fig. 65 indicating one spot with  $R_F \approx 0.4$ . It gives a light-yellow colour with ninhydrin. It gives negative results with  $\text{AgNO}_3$  and therefore cannot be formic acid. Nor does it smell of acetic acid. The infrared spectrum from the ammonium salt indicates that it is not a pure substance. It contains carboxylic groups.

### 7.4.5 Collection of Acids in Situ

The preceding experiments have indicated that low

molecular acids probably exist in peat water and that they are difficult to isolate due to interaction with other molecules.

One way of collecting the low molecular acids might be to use anion exchanger masses surrounded by a dialysing cellophane membrane mounted in situ in flowing peat water. The membrane will only permit the penetration of molecules up to a moderate molecular weight (about 500). If the equipment is mounted in an interminable source of acid, the chances of collecting an analysable amount of acids should be good. For this reason cellophane dialysing tubes were filled with 250 g anion exchange resin IRA 410  $\text{CO}_3^{2-}$  and the apparatus was mounted in situ in Morsta. The collection time was one week, after which the masses were brought to the laboratory. They were eluted, one with 1N HCl and one with 1N HCOOH. The eluates were evaporated and examined with paper chromatography.

As can be seen in Fig. 66 about the same results were obtained as in Ch. 7.4.2.1 when peat water was percolated through the ion exchangers. The hydrochloric acid eluate contained iron and apparent amounts of acids of the type seen in Fig. 54. Also in this case there were hardly any acids in the formic acid eluate. When the chromatograms were sprayed with ninhydrine, typical spots indicating amino acids appeared.

### 7.4.6 Examination of Artesian Water from Munkedal

Water was collected at Munkedal in Bohuslän, southwestern Sweden, from the bottom sand layer in a 17 m deep clay profile containing also quick clay with a sensitivity of more than 400.

5 litres of this artesian water were evaporated. A white unctuous residue was obtained. This was saponified and treated according to Sundgrén & Rauhala (1957) (Ch. 7.3.4). The methylesters obtained were examined by thin-layer chromatography. The result can be seen in Fig. 67. The evaporation residue of such a water contains fatty substances in small amounts.

To begin with it was thought in this investigation that substances in relatively unchanged form would diffuse

from the water into the clay and cause a quick clay formation. The results obtained indicate, however, that the quick clay forming process is of a more complicated chemical microbiological nature.

#### 7.4.7 Experiments with Clay Wax from Vesten

At Vesten a slide of relatively small extent occurred in 1960 and great amount of quick clay was exposed. Here it was easy to obtain high sensitive clay (quick clay), probably somewhat aged, in quantities desired. This material was used for experiments to break up the dispersing substances of the fatty acid type into individuals. When the material was extracted in a Soxhlet apparatus with benzene-ethanol (9-1), about 0.1 g bitumen per 100 g dried clay was obtained.

250 kg of the quick clay material was dried and pulverized. It was then sent to the Peat and Oil Laboratory in Helsinki and leached with benzene-ethanol in the peat bitumen apparatus (Sundgrén & Rauhala, 1965). The amount of bitumen obtained was, however, only about 5 grams, because the solvent did not penetrate the mass very well.

The bitumen was then treated in the same laboratory, as described in Ch. 7.3.4. The methylesters obtained were dissolved in a small amount of carbon tetrachloride and allowed to pass a column of aluminium-oxide type Brockman activity 1 (Fluka). The column was first eluted with  $\text{CCl}_4$ , which removed the substances with higher  $R_F$ -values. After that it was eluted with  $\text{CHCl}_3$ , which removed the fatty acid methylesters. For purity, they were tested by means of thin-layer chromatography.

The purified methylesters were subjected to gas chromatography in a Perkin Elmers Fractometer, type F6, with hydrogen flame detector, column Q, apiezon packing, temperature  $250^\circ\text{C}$ .

The chromatograms showed the existence of several aliphatic fatty acids. Owing to disturbances from impurities it has only been possible to ascertain a few fatty acids, viz. with 14, 16 and 18 carbon atoms. Also other acids seem, however, to be present.

#### 7.4.8 Discussion

The experiments in Ch. 7 indicate the possibility of analysing dispersing agents in nature by the use of ion exchangers. Great experimental difficulties occur, however, because different results are obtained due to varying treatment. The presence of iron in particular disturbs the fractionating. On the other hand, ion exchangers have proved very effective in disintegrating the complicated dispersing agents in simple substances. These results are similar to those obtained by Thomas (1962), i.e. in an anion column a decomposition of the complex material in ethers, aliphatic esters and other weakly ionized substances occurs. The experiments have shown that further fractionating with organic solvents isolate some of them. Much work remains, however, before complete fractionation can be made and this is a further work in advanced organic chemistry. With regard to the main problem the detailed composition of the dispersing agents cannot lead to an understanding of the processes taking place in situ. The investigations made, however, have given a good orientation in the problem and directed the investigation along new lines (Söderblom, 1974).

Also in recent years works have been published dealing with identifiable organic substances, both volatile and non-volatile, e.g. Naucke, Laaser & Tarkmann (1972). They have investigated substances suspected of being build-up components in dispersing agents such as furfural, benzaldehyde, gallic acid (cf. Ch. 5 and 6), pyrogallol, etc. Furthermore they have used thin-layer chromatography and everything indicates that this method will very soon be still further developed. Also papers treating fatty acids in soil have been published (e.g. Wang, Liang & Shen, 1969), where the results are in accordance with those of the present Author.

Of special interest is the fact, that fatty acids appear in soil and peat in homologous series. This indicates that the other dispersing agents will also occur in similar series.

The experiments in this chapter (7) have shown that there is no single substance causing the quick clay formation, rather large groups of substances have this effect. This is also in accordance with the fact

that quick clay can show such different properties, e.g. varying rapidity and different ageing effects. Probably the most rapid clay materials contain the simplest decomposition products from grass, etc., and reaction products from infiltrated substances. The "slow quick clays" seem to contain very complex substances some of them having a cementing effect.

One important group of dispersing agents is the synthetic detergents, which hitherto have not been

sufficiently investigated in connection with quick clay problems, because it has not been expected to find them in clayey soils. Detergents cannot be formed by natural processes. The investigations in the Jordbro slide (Söderblom, 1974) gave obvious analysis results that these substances must be of great importance in the quick clay forming process.

The existence of instable organic substances agrees well with the theory of ageing effect (cf. e.g. Glick, 1936).

## 8. GENERAL CONCLUSIONS

Archive studies of a number of geotechnical reports at the Institute showed that so called quick clays in Sweden occur both in typical marine clays and in varved clays sedimented in almost fresh water. This indicates that a marine sedimentation environment is not a necessary condition for the formation of a quick clay in situ. A simple sea-water salt-coagulation and subsequent leaching cannot reasonably be the primary factor causing quick clay formation in Sweden, especially with regard to the Donnan effect. It has been proved that quick clays always have a low salt content in their pore water but this can also apply to clays with a low sensitivity.

Laboratory experiments have shown that it is possible to transform, by means of dispersing agents, both marine (salt-water deposited) and varved (fresh-water deposited) clays into high sensitive clays (quick-clays).

A destruction of the organic material with hydrogen peroxide eliminates the typical quick clay properties and changes the pore water composition. This indicates the importance of organic material in different forms.

Certain organic materials act as cementing agents giving the clay a stable gel structure. Furthermore, a precipitation of organic materials in the clay gel can give a fissured system which is of importance to the local permeability properties. This allows a ground water recomposition in the quick clays which in turn is of importance when discussing the chemical stability of the clay properties, e.g. the delayed ageing effect in situ.

The third action of organic materials found, which is of special importance to the quick clay process, is its ability to act as dispersing agents giving the clay particles an increased negative charge.

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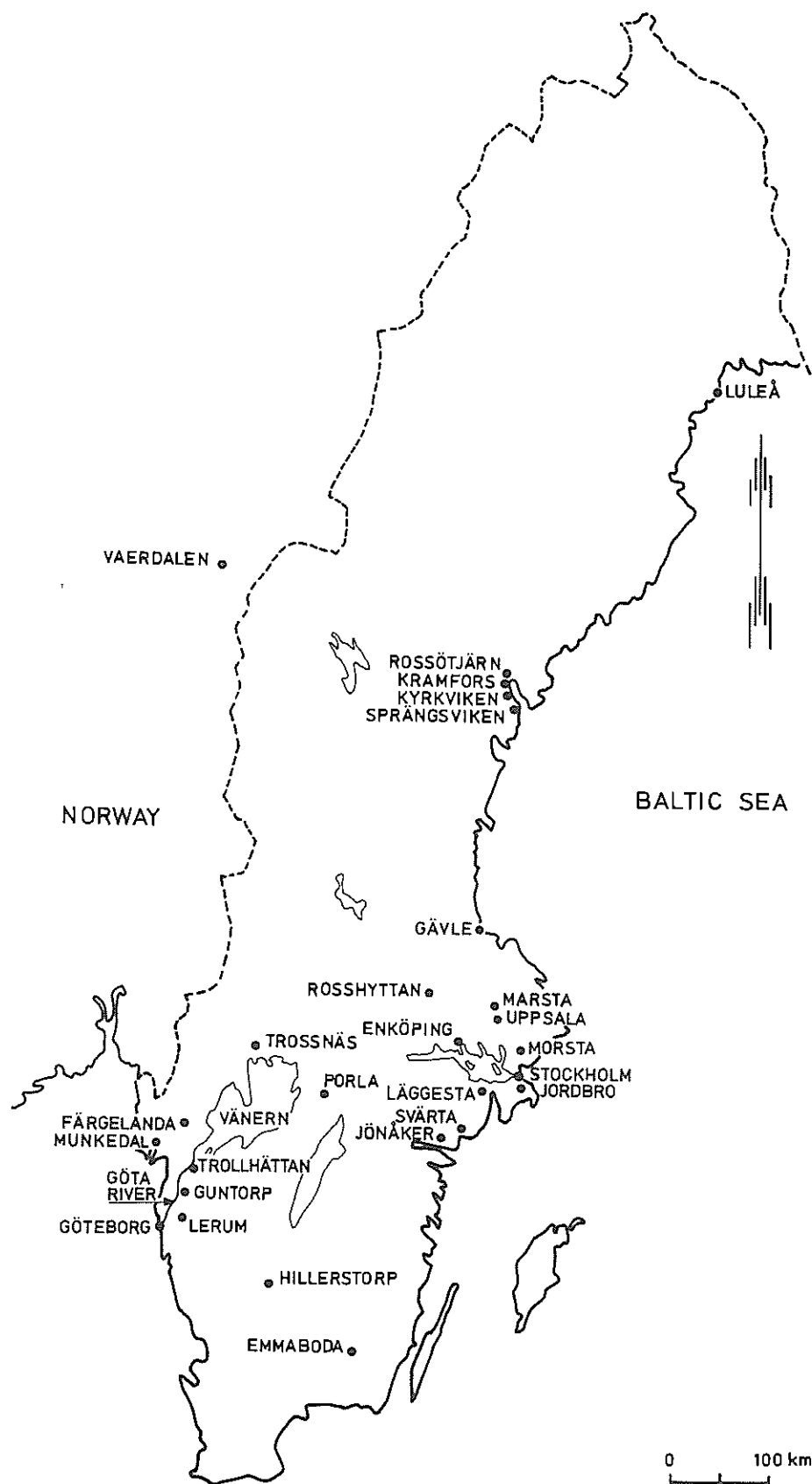
Rolf Söderblom



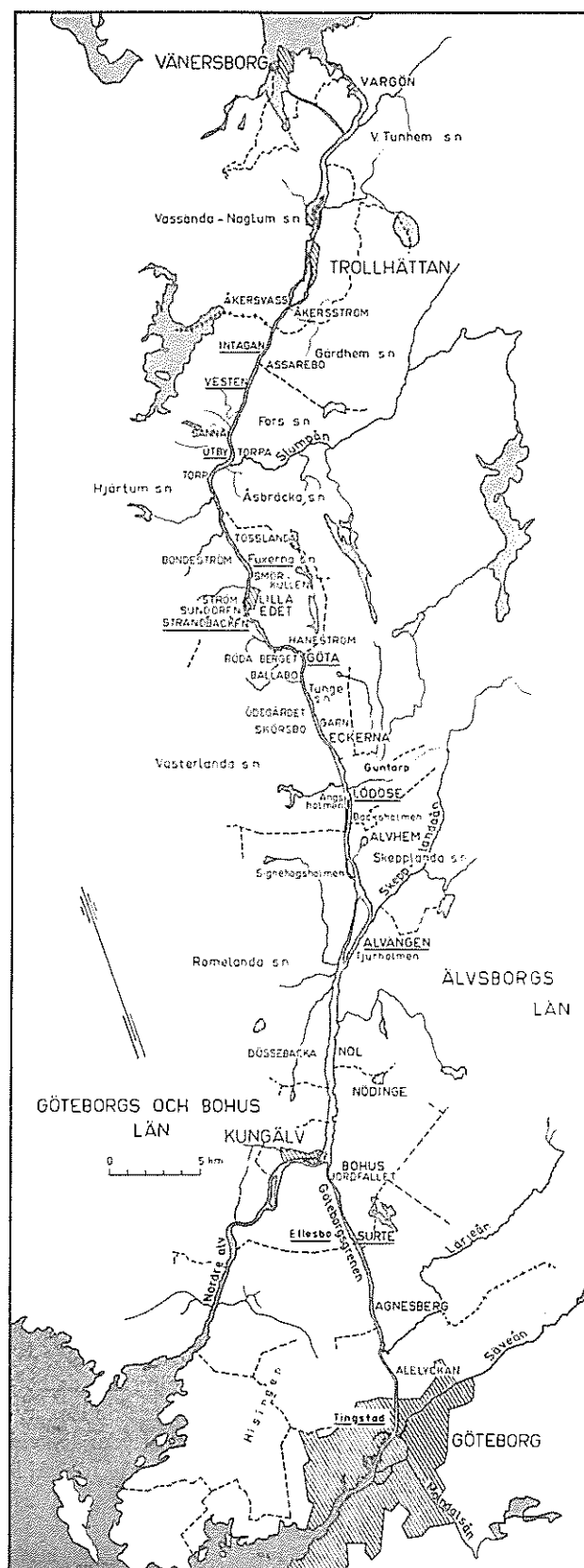
## APPENDICES







Appendix 1 Map of Sweden showing places investigated



Appendix 2 Map showing places investigated in the Göta River Valley (after Sundborg & Norrman, 1963. SGU Ser. Ca No. 43)

Site	Location (cf. App. 1 and 2)	Material investigated			Sedi- men- tation milieu	Examinations made		Remarks
		Quick clay	Normal clay	Peat water		Salt sound- ing	Sampling and lab. tests	
<u>Göta River Valley</u>								
Ellesbo	About 14 km N Göte- borg	x	x		Marine	x	x	
Fuxerna	Near the center of Lilla Edet	x	x		"	x	x	
Göta	About 4 km SSE Lilla Edet	x	x		"	x	x	
Intagan	About 5 km SSW Trollhättan	x	x		"	x	x	Salt soundings in slide scar from 1648
Lödöse	About 12 km S Lilla Edet	x	x		"	x		Investigations on the football ground
Strandbacken	Near Lilla Edet	x	x		"	x	x	
Surte	About 13 km N Göte- borg	x	x		"	x	x	
Tingstad	Near the center of Göteborg		x		"			Results from the Göta River investigations
Utby	About 11 km SSW Trollhättan	x	x		"	x	x	
Vesten	About 8 km SSW Tollhättan	x	x		"		x	
Älvängen	About 30 km NNE Göteborg		x		"	x		
<u>Other sites</u>								
Enköping	About 80 km WNW Stockholm		x		Marine and non- marine	x	x	
Färgelanda	About 40 km NNW Trollhättan	x	x		Marine	x	x	Sewage
Jordbro	About 20 km S Stockholm	x	x		Non- marine	x	x	Slide in 1972. Sewage. Remote sensing
Jönåker	About 120 km SW Stockholm	x	x		Marine and non- marine			Remote sensing
Kramfors	About 400 km N Stockholm				Marine			Remote sensing. Slide in 1962
Kungsängen	In Uppsala	x			"	x	x	
Kyrkviken	About 1 km S Kram- fors							Remote sensing
Läggesta	About 50 km SSW Stockholm							Remote sensing
Morsta	About 32 km NNE Stockholm			x	Non- marine		x	
Munkedal	About 40 km NW Trollhättan	x	x	x	Marine			Artesian water
Porla	About 5 km NNE Laxå (half way Stockholm-Göte- borg)			x				Ochre from the "Old Spring of Porla" Berzelius
Rosshyttan	About 150 km NW Stockholm (on the railroad line Sala- Krylbo)	x	x	x	Non- marine		x	Distance according to the State Railway 147+500 V12

Appendix 3 Test sites and indication of investigations made  
(Continued on next page)

Site	Location (cf. App. 1 and 2)	Material investigated			Sedi- men- tation milieu	Examinations made		Remarks
		Quick clay	Normal clay	Peat water		Salt sound- ing	Sampling and lab. tests	
Rossötjärn	About 2 km N Kramfors							
Skå-Edeby	About 18 km W Stockholm		x		Marine and non- marine	x	x	On an island in Lake Mälaren
Sköttorp	About 40 km ENE Trollhättan				Marine			Slide in 1946
Sprängsviken	About 9 km S Kramfors							Remote sensing
Svärta	About 100 km SW Stockholm	x	x		Marine and non- marine			Slide in 1939. Remote sensing
Trossnäs	About 12 km WNW Karlstad	x	x		"			Slide in 1968. Remote sensing. Sewage
Vassända Naglum	About 7 km N Trollhättan	x	x		Marine	x	x	Sewage

Appendix 3 Test sites and indication of investigations made

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## ACIDS

Solvent: If nothing else is said the solvent used is butanol - formic acid - water (4:1:5).

All acids are analysed in four concentrations, 30, 21, 12 and 1  $\mu$ l of concentrate.

Standards: If nothing else is said the standards are tartaric, malic and lactic acids ( $R_F \approx 0.22, 0.45, 0.67$  respectively).

Spray: If nothing else is said bromophenolblue.

The  $R_F$ -values of the unknown substances are calculated adopting that the  $R_F$ -value of lactic acid is 0.67 exactly.

Fig. 26.

Standard: Oxalic, malic and lactic acid (tail 0.45, 0.67).

1.  $R_F \approx 0.03 - 0.04$  Well formed spot. Also visible with the spray reagents  $K_3Fe(CN)_6 - FeCl_3$ .
2.  $R_F \approx 0.08 - 0.23$ . Tailing spot.
3.  $R_F \approx 0.26 - 0.45$ . Tailing spot. Will at lower concentrations be divided into two spots with  $R_F \approx 0.23$  and 0.29 at the lowest concentration.

Fig. 28.

1.  $R_F \approx 0.00 - 0.02$ . Well formed spot.
2.  $R_F \approx 0.05$ . Well formed spot.
3.  $R_F \approx 0.12$ . Well formed spot.
4.  $R_F \approx 0.18 - 0.38$ . Tail forming spots. Will separate into two spots at lower concentrations.

Fig. 29.

Standard: Oxalic acid (tail), malic and lactic acid.

1.  $R_F \approx 0.09$ . Well formed spot.
2.  $R_F \approx 0.13$ . Well formed spot.
3.  $R_F \approx 0.19 - 0.28$ . Somewhat tail forming substance. Will form a well defined spot with  $R_F \approx 0.22$  at lower concentrations.
4.  $R_F \approx 0.31$ . Well defined spot.
5.  $R_F \approx 0.65$ . Well formed spot. Can be lactic or succinic acid.

Fig. 30.

1.5 m.

1.  $R_F \approx 0.01$ . Well defined spot.
2.  $R_F \approx 0.06$ . Well defined spot.
3.  $R_F \approx 0.13$ . Well defined spot.
4.  $R_F \approx 0.19$ . Well defined spot.
5.  $R_F \approx 0.24$ . Well defined spot.

2.0 m.

1.  $R_F \approx 0.06$ . Well defined spot.
2.  $R_F \approx 0.13$ . Well defined spot.

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Fig. 30 - 2.0 m.

3.  $R_F \approx 0.18$ . Well defined spot.

4.  $R_F \approx 0.23$ . Well defined spot.

2.5 m.

1.  $R_F \approx 0.01$ . Well defined spot.

2.  $R_F \approx 0.08$ . Very weak spot, well defined.

3.  $R_F \approx 0.12$ . Well defined spot.

4.  $R_F \approx 0.18$ . Very weak well defined spot.

5.  $R_F \approx 0.24$ . Very weak well defined spot.

Contact:

1.  $R_F \approx 0.01$ . Well defined spot.

2.  $R_F \approx 0.06$ . Very weak well defined spot.

3.  $R_F \approx 0.12$ . Well defined spot.

4.  $R_F \approx 0.16 - 0.26$ . Tail forming spot.

5.  $R_F \approx 0.22 - 0.31$ . Tail forming spot.

6.  $R_F \approx 0.65$ . Well defined spot. Can be lactic acid.

3.0 m.

1.  $R_F \approx 0.06$ . Very weak well formed spot.

2.  $R_F \approx 0.12$ . Weak well formed spot.

3.  $R_F \approx 0.18$ . Well defined spot.

4.  $R_F \approx 0.24$ . Well defined spot.

3.5 m.

1.  $R_F \approx 0.06$ . Well formed spot.

2.  $R_F \approx 0.12$ . Well formed spot.

3.  $R_F \approx 0.19$ . Very diffuse spot.

4.  $R_F \approx 0.25$ . Very diffuse spot.

4.0 m.

1.  $R_F \approx 0.00$ . Well defined spot.

2.  $R_F \approx 0.06$ . Weak well defined spot.

3.  $R_F \approx 0.13$ . Weak well defined spot.

4.  $R_F \approx 0.18$ . Weak well defined spot.

5.  $R_F \approx 0.24$ . Very weak well defined spot.

4.5 m.

1.  $R_F \approx 0.06$ . Well formed spot.

2.  $R_F \approx 0.11$ . Well formed relatively weak spot.

3.  $R_F \approx 0.18$ . Well formed spot.

4.  $R_F \approx 0.24$ . Well formed spot.

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Fig. 31.

2.0 m.

1.  $R_F \approx 0.01$ . Well defined spot.
2.  $R_F \approx 0.04$ . Well defined spot.
3.  $R_F \approx 0.09$ . Well defined spot.
4.  $R_F \approx 0.12$ . Well defined spot.
5.  $R_F \approx 0.13 - 0.30$ . Tail.
6.  $R_F \approx 0.30 - 0.34$ . Tail.
7.  $R_F \approx 0.22 - 0.43$ . Tail.
8.  $R_F \approx 0.68$ . Can be lactic acid. Well defined spot.

3.0 m.

1.  $R_F \approx 0.03$ . Will at lowest concentration be divided up into three spots with  $R_F \approx 0.01$ ,  $0.03$  and  $0.05$ .
2.  $R_F \approx 0.07$ . Spot with tail forming tendency.
3.  $R_F \approx 0.11 - 0.31$ . Tail.
4.  $R_F \approx 0.28 - 0.42$ . Tail.
5.  $R_F \approx 0.18 - 0.49$ . Tail.
6.  $R_F \approx 0.64$ . Well formed spot. Can be lactic acid.

4.0 m.

1.  $R_F \approx 0.01$ . This spot joins spot 2. Gives positive reaction of phosphoric acid.
2.  $R_F \approx 0.03$ . Well defined spot. Will join spot 3.
3.  $R_F \approx 0.06$ . Small well formed spot.
4.  $R_F \approx 0.08$ . Small well formed spot.
5.  $R_F \approx 0.10$ . Well formed spot.
6.  $R_F \approx 0.13$ . "Half spot". Will join spot 5.
7.  $R_F \approx 0.13 - 0.27$ . Tail forming spot.
8.  $R_F \approx 0.28$ . Small spot.
9.  $R_F \approx 0.16 - 0.35$ . Tail.
10.  $R_F \approx 0.50$ . Small well formed spot.
11.  $R_F \approx 0.66$ . Well formed spot. Can be lactic acid.

Spot 1 - 8 are visible in different red yellow colours when sprayed with ninhydrin. The tail 9 and spots 10, 11 not visible.

This chromatogram illustrates the very complex composition of the Ellesbo fractions.

5.0 m.

1.  $R_F \approx 0.00$ . Well formed spot. Positive reaction on phosphoric acid.
2.  $R_F \approx 0 - 0.47$ . Tail. Will divide up at lower concentration.
3.  $R_F \approx 0.30$ . Tail forming spot.
4.  $R_F \approx 0.70$ . Well formed spot. Can be lactic acid.

At the lowest concentration the tail will divide up to four spots with  $R_F \approx 0.11$ ,  $0.16$ ,  $0.23$  and  $0.29$ .

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Fig. 31

6.0 m.

1.  $R_F \approx 0.00$ . Very weak well defined spot. Positive reaction on phosphoric acid.
2.  $R_F \approx 0.11$ . Weak well defined spot.
3.  $R_F \approx 0.15 - 0.27$ . Acid area. The acid substances seem to have flown around in the paper.
4.  $R_F \approx 0.20 - 0.32$ . Acid area. The same conclusions as in 3.
5.  $R_F \approx 0.51 - 0.66$ . Seems to be disturbances in the chromatogram.
6.  $R_F \approx 0.67$ . Well defined spot. Can be lactic acid.

7.0 m.

1.  $R_F \approx 0.01$ . Well defined spot.
2.  $R_F \approx 0 - 0.23$ . Tail.
3.  $R_F \approx 0.13 - 0.39$ . Tail. At concentration  $7 \times 3 \mu\text{l}$  will divide up into two tails.
4.  $R_F \approx 0.66$ . Well defined spot. Can be lactic acid.

At the lowest concentration the tails will divide up into four spots with  $R_F \approx 0.03, 0.09, 0.17$  and  $0.22$ .

8.0 m.

1.  $R_F \approx 0.01$ . Well defined spot.
2.  $R_F \approx 0.06$ . Well defined spot.
3.  $R_F \approx 0.11$ . Well defined spot.
4.  $R_F \approx 0.14 - 0.30$ . Acid area. The acid substances seem to have flown round in this paper.
5.  $R_F \approx 0.24 - 0.42$ . Acid area. As in 4.
6.  $R_F \approx 0.66$ . Well formed spot. Can be lactic acid.

9.0 m.

1.  $R_F \approx 0.06$ . Well formed very weak spot.
2.  $R_F \approx 0.17$ . Well formed spot.
3.  $R_F \approx 0.20 - 0.29$ . Tail forming spot.
4.  $R_F \approx 0.30 - 0.35$ . Tail forming spot.
5.  $R_F \approx 0.37$ . Extremely weak spot.
6.  $R_F \approx 0.68$ . Well formed spot. Can be lactic acid.

Artesian water.

1.  $R_F \approx 0.04$ . Well defined spot.
2.  $R_F \approx 0.12$ . Spot being part of a tail.
3.  $R_F \approx 0 - 0.35$ . Tail.
4.  $R_F \approx 0.33$ . Well defined strong spot in the middle of the tail. Clearly visible. Gives negative reaction on phosphoric acid.
5.  $R_F \approx 0.24 - 0.44$ . Tail.

Fig. 34.

1.  $R_F \approx 0.06$ . Well defined spot.
  2.  $R_F \approx 0.08$ . Well defined spot. Contains iron, will give red colour with KSCN.
  3.  $R_F \approx 0.10$ . Well defined spot.
  4.  $R_F \approx 0.13$ . Well defined spot. Contains iron, will give red colour with KSCN.
-



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Fig. 34

5.  $R_F \approx 0.19$ . Well defined spot.

6.  $R_F \approx 0.19 - 0.39$ . Tail forming spot.

Fig. 35.

Standard: Oxalic acid (tail), malic- and lactic acid.

1.  $R_F \approx 0.14$ . Contains iron. Absorbs UV. Coloured red by KSCN.

2.  $R_F \approx 0.17 - 0.35$ . Tail forming spot. Will be divided into two spots at lower concentrations.

Fig. 36.

1.  $R_F \approx 0.15 - 0.27$ . Somewhat tail forming spot. Gives a well formed spot at the lowest concentration with  $R_F \approx 0.20$ . Can be the acid proposed by Schreiner and Shorey but model substance impossible to obtain at present.

Fig. 38.

1.  $R_F \approx 0.48$ . Well defined spot. Seems to correspond to acid found by Ramaut (regarding experimental errors).

2.  $R_F \approx 0.66$ . Well defined spot.

Fig. 42.

1.  $R_F \approx 0.06$ . Well formed spot.

2.  $R_F \approx 0.10 - 0.22$ . Will at lower concentrations split up into two relatively well defined spots with  $R_F \approx 0.12$  and  $0.16$ .

3.  $R_F \approx 0.19 - 0.30$ . Will at lower concentrations split up into two relatively well defined spots with  $R_F \approx 0.21$  and  $0.26$ .

4.  $R_F \approx 0.74$ . Well formed spot.

Fig. 43.

1.  $R_F \approx 0.06$ . Well formed spot.

2.  $R_F \approx 0.11$ . Well formed spot.

3.  $R_F \approx 0.14 - 0.26$ . Tail forming spot.

4.  $R_F \approx 0.24 - 0.35$ . Tail forming spot. Will divide into two spots with  $R_F \approx 0.25$  and  $0.29$  at lower concentration.

Fig. 44.

1.  $R_F \approx 0.03$ . Well defined spot.

2.  $R_F \approx 0.09$ . Well defined spot.

3.  $R_F \approx 0.17$ . Well defined relatively weak spot.

4.  $R_F \approx 0.24$ . Well defined spot.

Fig. 46.

1.  $R_F \approx 0.00$ . Well formed spot.

2.  $R_F \approx 0.05$ . Weak spot, well defined.

3.  $R_F \approx 0.10$ . Well defined spot. Contains iron.

4.  $R_F \approx 0.16$ . Well formed spot. Contains iron. Can be the "iron spot" in  $\text{FeCl}_3$ .

5.  $R_F \approx 0.18 - 0.38$ . Tail forming spot.

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Fig. 47.

1.  $R_F \approx 0.11$ . Well defined spot.
2.  $R_F \approx 0.15$ . Well defined spot.
3.  $R_F \approx 0.72$ . Well defined very distinct spot.

Fig. 48.

1.  $R_F \approx 0.13 - 0.41$ . Tail. Absorbs weakly in UV. Gives weak positive reaction with the spray reagent for phosphoric acid.

Fig. 49.

1.  $R_F \approx 0.00$ . Well defined spot.
2.  $R_F \approx 0 - 0.03$ . Weak tails.

Fig. 50.

1.  $R_F \approx 0.00$ . Well defined spot.
2.  $R_F \approx 0.00 - 0.05$ . Weak tail.
3.  $R_F \approx 0.11$ . Well defined spot.
4.  $R_F \approx 0.15$ . Well defined spot.
5.  $R_F \approx 0.17 - 0.24$ . Weak tail.

Fig. 51.

1.  $R_F \approx 0.05$ . Well defined spot.
2.  $R_F \approx 0.07$ . Somewhat tail forming spot.
3.  $R_F \approx 0.01 - 0.40$ . Tail.

Fig. 54.

1.  $R_F \approx 0.05$ . Well formed spot.
2.  $R_F \approx 0.10$ . Well formed spot.
3.  $R_F \approx 0.14 - 0.26$ . Tail.
4.  $R_F \approx 0.28$ . Tail forming spot.

Fig. 55.

1.  $R_F \approx 0.17$ . Very weak spot.

Fig. 56.

1.  $R_F \approx 0.03$ . Well formed spot.
2.  $R_F \approx 0.08$ . Somewhat tail forming spot.
3.  $R_F \approx 0.15$ . Somewhat tail forming spot.
4.  $R_F \approx 0.19$ . Well formed spot.
5.  $R_F \approx 0.24$ . Weak well defined spot.
6.  $R_F \approx 0.28$ . Well defined spot. Gives positive reaction of phosphoric acid. Has somewhat lower  $R_F$  than ortho-phosphoric acid (0.33).

Fig. 59.

1.  $R_F \approx 0.06$ . Well formed spot.
  2.  $R_F \approx 0.47$ . Well formed spot.
  3.  $R_F \approx 0.73$ . Well formed spot.
- None of the acids contains iron or phosphoric acid.
-

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Fig. 60.

1.  $R_F \approx 0.13$ . Well defined spot.

Fig. 61.

1.  $R_F \approx 0.11$ . Well defined spot.
2.  $R_F \approx 0.15$ . Well defined spot.
3.  $R_F \approx 0.17 - 0.26$ . Tail forming relatively well shaped spot.

Fig. 62.

1.  $R_F \approx 0.10$ . Well defined very weak spot.
2.  $R_F \approx 0.21$ . Somewhat tail forming spot.

Fig. 63.

1.  $R_F \approx 0.03$ . Well formed spot.
2.  $R_F \approx 0.09$ . Well formed spot.
3.  $R_F \approx 0.13$ . Probably tail forming spot.
4.  $R_F \approx 0.14 - 0.28$ . Tail forming spot.
5.  $R_F \approx 0.35 - 0.43$ . Tail.  
Gives positive reaction for phosphoric acid.
6.  $R_F \approx 0.76$ . Well formed spot.

Fig. 66.

1.  $R_F \approx 0.00$ . Well formed spot.
2.  $R_F \approx 0.65$ . Well formed spot.
3.  $R_F \approx 0.09$ . Well formed spot. Contains iron.
4.  $R_F \approx 0.16$ . Well formed spot. Contains iron.
5.  $R_F \approx 0.18 - 0.38$ . Tail.

Fig. 65. Analysed as ammonium salts.

Solvent: Ethanol - ammonia 100:1.

Standard: Ammonium acetate. ( $R_F \approx 0.33$ )

Spray: Bromophenolblue.

1.  $R_F \approx 0 - 0.06$ . Weak tail coloured by ninhydrin.
2.  $R_F \approx 0.31$ . Well formed spot. Yellow coloured by ninhydrin. Gives negative reaction of formic- and acetic acid.

Fig. 41, 52, 57, 67. Thin layer chromatograms. Substances see the figures. Analysed as methylesters.

Solvent: Petrol ether - diethylether (70 - 30).

Analysed in concentrations  $1 \times 5 \mu\text{l}$ .

Standard: Palmitic acid, methyl ester.

Spray: Dichromate sulphuric acid.

Found: See each figure. Only the "fatty" spots of interest in this investigation.

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## AMINO ACIDS

Solvent: If nothing else is said the solvent used is butanol, acetic acid - water (4:1:5).

The amino acids are analysed in 4 concentrations 30, 21, 12 and 3  $\mu$ l.

Standard: Glutaminic acid,  $\alpha$ -alanine, leucine ( $R_F \approx 0.30, 0.38, 0.73$ ).

Spray: Ninhydrine.

Fig. 45.

1.  $R_F \approx 0.09$ . Well formed spot. Probably a peptide.
2.  $R_F \approx 0.26$ . Well defined unidentified spot.
3.  $R_F \approx 0.29$ . Well defined spot. Can be glutamic acid.
4.  $R_F \approx 0.32$ . Well defined spot. Can be  $\alpha$ -alanine.
5.  $R_F \approx 0.38$ . Well formed spot.
6.  $R_F \approx 0.55$ . Well formed spot. Can be valine.
7.  $R_F \approx 0.71$ . Well formed spot. Can be leucine.

Fig. 53.

Standard: Glutamic acid,  $\alpha$ -alanine leucine.

1.  $R_F \approx 0.06 - 0.11$ . Tail.
2.  $R_F \approx 0.21$ . Well defined spot.
3.  $R_F \approx 0.45$ . Tail forming spot (uncertain  $\alpha$ -alanine).

Fig. 58.

1.  $R_F \approx 0.06$ . Weak spot.
2.  $R_F \approx 0.21$ . Well defined spot.
3.  $R_F \approx 0.29$ . Well formed spot can be glutamic acid.
4.  $R_F \approx 0.35$ . Well formed spot can be  $\alpha$ -alanine.
5.  $R_F \approx 0.46$ . Well formed spot.
6.  $R_F \approx 0.56$ . Well formed spot can be valine.
7.  $R_F \approx 0.75$ . Well formed spot can be leucine.

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## POLYPHENOLS

Solvent: If nothing else is said the solvent used is 2% HAc - water.

If nothing else is said the polyphenols are analysed in 4 concentrations 30, 21, 12 and 3  $\mu$  l.

Standard: None if nothing else is said.

Spray: 1%  $\text{FeCl}_3$  1%  $\text{K}_3\text{Fe}(\text{CN})_6$ .

Fig. 27.

Analysed in 2 concentrations. Standard: Gallic acid.

Acetone extract.

1.  $R_F \approx 0.45$ . Tail forming spot.

2.  $R_F \approx 0.51 - 0.68$ . Tail.

Water extract.

3.  $R_F \approx 0.54 - 0.67$ . Tail.

Fig. 33.

Solvent: butanol - acetic acid-water (4:1:5).

1.  $R_F \approx 0.43 - 0.62$ . Tail, contains iron. (Visible with  $\text{KSCN}$ ,  $(\text{NH}_4)_2\text{S}$ ).

Fig. 37

1.  $R_F \approx 0.12$ . Tail.

2.  $R_F \approx 0.12 - 0.41$ . Tail.

3.  $R_F \approx 0.41 - 0.76$ . Tail.

Fig. 39.

1.  $R_F \approx 0 - 0.46$ . Tail.

2.  $R_F \approx 0.49$  area with several spots covering each other.

Fig. 40.

$R_F \approx 0.63 - 0.92$ . Tail. Will at lowest concentration form a well defined spot with  $R_F \approx 0.68$ .

Fig. 64.

1.  $R_F \approx 0 - 0.14$ . Tail.

2.  $R_F \approx 0.14 - 0.55$ . Tail.

3.  $R_F \approx 0.30$ . Well defined spot.

4.  $R_F \approx 0.38$ . Well defined spot.

5.  $R_F \approx 0.45$ . Well defined spot.

At the lowest concentrations five well formed spots with  $R_F \approx 0.00, 0.05, 0.09, 0.17$  and  $0.31$  are seen.



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