BALTIC MARINE BIOLOGISTS

RECOMMENDATIONS ON METHODS
FOR MARINE BIOLOGICAL STUDIES
IN THE BALTIC SEA

Edited by

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SECTION 4

SEDIMENT DESCRIPTION

INTRODUCTION

A sediment can be described in many different ways. This has also been the case in Baltic research, due to the many different types of scientific investigations performed in the area. The present recommendations aim to give a basic set of simple but representative parameters. They should be meaningful to geologists as well as biologists so that all scientists working with modern Baltic sediments use identical methods and obtain comparable results. It is hoped that the recommended parameters thus may serve as a "common language" for all scientists working with Baltic sediments. Many geologists and geochemists also use more sophisticated methods of describing a sediment. These methods are often very time consuming and/or demand advanced instrumentation. Scientists using such sophisticated methods are asked to report their results together with the basic parameters recommended here.

Sieving of the sediment has not been included among the recommended parameters. There are several reasons for this. It is time consuming and can hardly be done on board the ship. It can be done in many different ways (dry or wet sieving etc.) and a standardised sieving method demands expensive equipment. The granulometric description is believed not to be a sufficient method for an ecologist. Permeability and arrangement of the particles in the sediment are of greater importance and they are dependent on both grain size and packing of the sediment. A loosely packed sediment is more favourable for the microfauna than a well packed sediment, though they display the same granulometric graph. Shear strength measurements coupled with other recommended parameters will be an acceptable and time saving substitute for sieving.

Scientists interested in sieving methods and classification of sediments are referred to Casagrande (1948) and Kiff (1973).

The following recommendations are the result of correspondence within the working group, and discussions during two sediment symposia held at the Askö laboratory in 1972 and 1973, (Statens Naturvårdsverk 1973, 1974). The reports (in Swedish) can be obtained from The Research Secretariat, Environment Protection Board, Fack, S-171 20 Solna, Sweden.

RECOMMENDATIONS FOR THE DESCRIPTION OF BALTIC BOTTOM SEDIMENTS

1. Station Data

For information that should be given concerning sampling stations, see Section 1.
In this connection data on sampling gear (with literature reference to exact type),
speed of lowering of sampler (e.g. "free fall" or "1 m/s") and sea state at samp-
ling are of special importance.

2. Sediment Structure

A description of the visual appearance of the uppermost layers of the sediment
(down to 5 cm depth) should be given, as for instance tracks or burrows of animals,
content of algal pieces, presence of shell fragments, nodules, etc.

3. Colour

The colour of the sediment should be described according to a standard colour set,
the Rock Color Chart of the Geological Society of America (see below). The deter-
mination should be made on fresh samples, as little disturbed as possible, and
preferably in artificial light. Any layering of the uppermost 5-10 cm of the sedi-
ment should be carefully described. The recommended colour chart is based on
the widely used Munsell system. The colour names have been taken from the ISCC-
NBS system as described in U S National Bureau of Standards Research Paper
RP 1239, and this system has been accepted by a large number of scientific orga-
nizations. The rock colour chart can be ordered from: The Geological Society of
America, Attention: Miss Clara Tuthill, 3300 Penrose Place, Boulder, Colorado
80301, USA. The price in 1974 was 5 US$.

4. Loss of Weight on Heating

The amount of sediment used should correspond to at least 1 g of dry sediment.
The sediment should be taken in slices of a maximum of 2-2.5 cm thickness, down
to a depth of at least 5 cm (e.g. 0-2.5, 2.5-5 cm or 0-2, 2-4, 4-6 cm or even
thinner slices). The volume of the initial sample should, if possible, be so accura-
tely determined that the density of the sediment can be calculated. The final results
should be given in such a form that they can be accurately recalculated on a volume,
wet weight or dry weight basis, as may be desired for comparisons.

4.1   Water Content

The loss of weight of the fresh sediment, when heated to $80^{\circ}C$ to constant weight, is attributed to the water content. This, together with shear strength measurements, will indicate the content of friction and/or cohesion material in the sediment.

4.2   Loss on Ignition

After determination of water content at $80^{\circ}C$, the sediment should be incinerated at $500^{\circ}C$ to constant weight (at least 2 hours under good air exchange). It is very important that the temperature is checked with a calibrated thermometer. The upper temperature limit has been chosen high enough to allow combustion of organic matter, but low enough to avoid influence from dehydration of mica minerals. The loss of weight between $80^{\circ}C$ and $500^{\circ}C$ is often attributed to the organic content of the sediment, but for fine grained sediments some residual water may also be involved.

5.   Redox State

The redox state of the sediment should be measured as E_h, by means of a platinum and a reference electrode, as described in the article by Bågander (Appendix 4.1, page 37). The measurements should start in the free water, at least 1 cm above the sediment surface, and preferably continue to a depth of 10 cm, at 1 cm intervals or continuously. It takes some training to handle the electrodes and the sediment samples in a proper way, but it should be a routine method for all ecologists wanting to relate biological to chemical observations (see e.g. Fenchel 1969).

6.   Shear Strength

Shear strength should be measured by means of a vane shear apparatus, in situ by divers (Dill & Moore 1965), or in sediment samples. If sediment samples are used, large diameter corers or box grabs that disturb the sediment as little as possible should be used for the sampling. The van Veen is not suitable. The vane used should have a height-to-width ratio of 2.

The shear strength test is performed by driving a vane into the sediment and rotating it, while the resistance to rotation is measured. The shear strength is then calculated from the maximum torsional momentum thus obtained. The apparatus used for the test is called the vane-shear apparatus. One such vane-shear apparatus is

shown in Fig. 4.1. It has been developed by the Swedish State Geotechnical Institute, Stockholm, Sweden, and is manufactured by AB Nyttoverktyg, Trångsund, Sweden.

When the vane (1) has been lowered to the testing position the turning handle (2) is turned carefully at such a speed that the rate of rotation of the indicating scale (3) is kept constant. The indicator (4) will then move from zero to a position (in this case 3) where maximum sediment force is obtained. The value from the digital scale on the apparatus is then translated into maximum torsional momentum (M_{max}) from a calibration graph. The shear strength s is calculated from:

$$M_{max} = s \left(\pi \, DH \frac{D}{2} + 2 \frac{\pi D^2}{4} \cdot \frac{2}{3} \cdot \frac{D}{2} \right)$$

D = diameter of vane   H = height of vane

if H = 2D, which is recommended here

$$s = \frac{6}{7} \frac{M_{max}}{\pi D^3} = \frac{M_{max}}{C}$$

where C is a constant

For more detailed information the reader is referred to Cadling and Odenstad (1950), Jakobson (1954), Dill and Moore (1964), Inderbitzen et al. (1971) and Symposium on vane shear testing of soil (1957).

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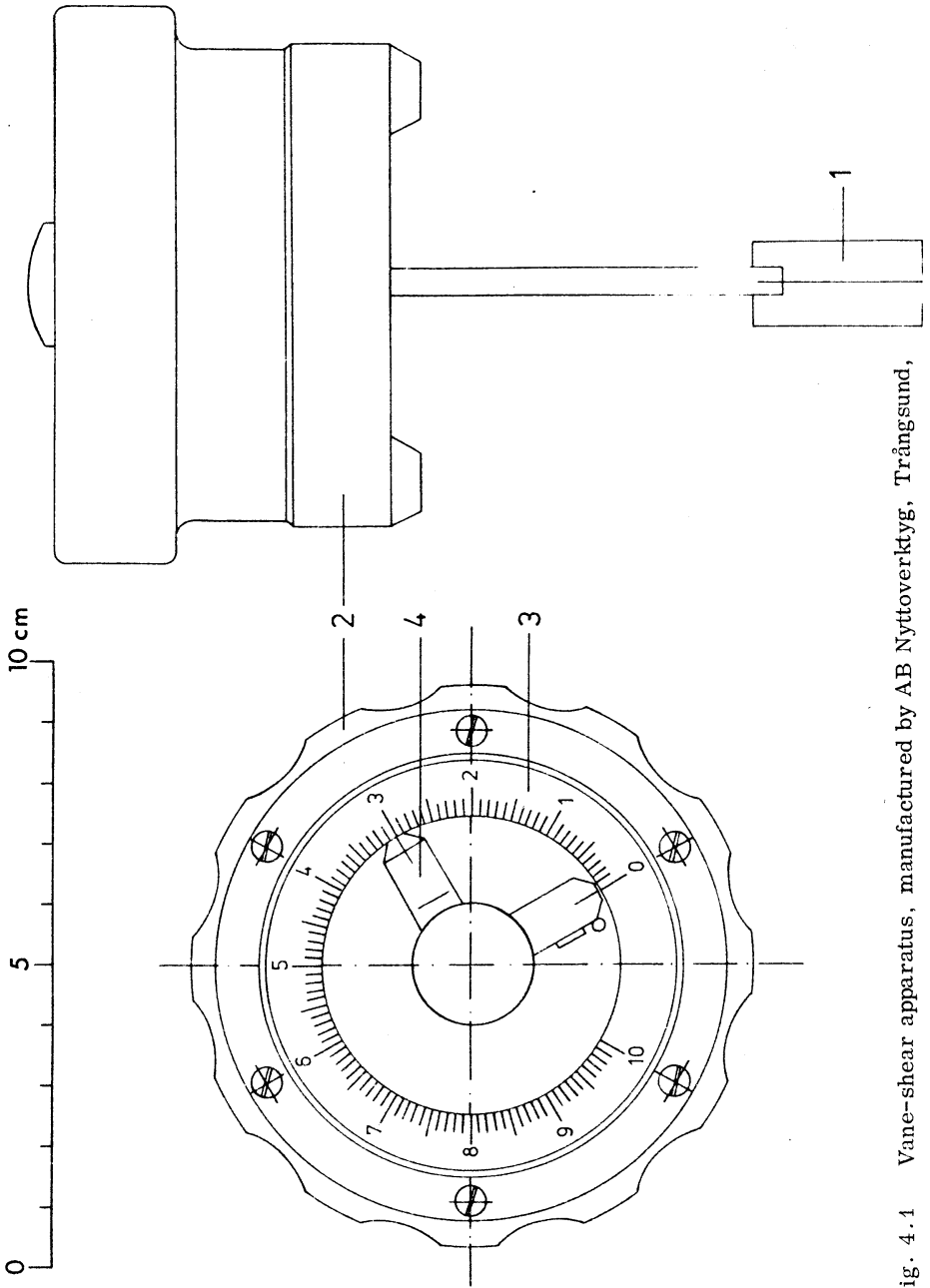Symposium on vane shear testing of soil. 1957. - Am. Soc. Test. Mat. spec. techn. Publ. No 193.

Fig. 4.1   Vane-shear apparatus, manufactured by AB Nyttoverktyg, Trångsund, Sweden. (1) Vane, (2) Turning handle, (3) Scale, (4) Indicator.

REDOX MEASUREMENTS IN NATURAL WATERS AND SEDIMENTS

by

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Redox Potential - Theory

A chemical process in which electrons are lost is called an <u>oxidation</u>. The opposite. a process in which electrons are gained is called a <u>reduction</u>. In chemical reactions an oxidation process is always coupled with a process in the opposite direction, a reduction, and vice versa

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^- \tag{I}$$

The reaction above is called a redox reaction. Fe(III) is the oxidized form and Fe(II) is the reduced form. The reaction is at equilibrium when one Fe(III) ion is reduced for every Fe(II) ion that is oxidized. At equilibrium the redox couple has a characteristic redox potential (E).

The voltage scale is relative and the reaction

$$H_2 \leftrightarrow 2H^+ + 2e^- \tag{II}$$

has been chosen as the standard zero point in this scale. The redox potential is therefore referred to as E_h. The reaction (I) has according to this scale a potential of +0.771 V. (The potential is given according to the international convention. Note that in American books, especially old ones, the potentials are given with the same numerical values, but opposite signs.)

The redox potential is measured by using an inert metal electrode (Pt or Au) in combination with a reference electrode (calomel or silver/silver chloride). When immersed in a solution and joined to a circuit they form an electrochemical cell. The EMF or cell potential can then be measured. Each of the electrodes is half cell for which the potential is given by the Nernst equation:

$$E = E^O + \frac{RT}{nF} \ln \frac{ox}{red} \qquad \text{(III)}$$

E^O = constant for the half cell

R   = gas constant (8.3143 houles/deg. and mole)

F   = Faradays constant (96.487 coulombs/equivalents)

n   = number of electrons involved, according to the formula

T   = absolute temperature

ox/red = activity ratio of the oxidizing and reducing species.

The potential of an electrochemical cell can be written:

$$E_{cell} = E_{right} - E_{left} \qquad \text{(IV)}$$

In this case when using a platinum electrode and a reference electrode we can write:

$$E_{cell} = E_h - E_{ref} \qquad \text{(V)}$$

What is really measured is the difference in potential between the two electrodes.

The redox potential is an <u>intensity</u> factor like pH and temperature and gives no information on either the oxidizing or the reducing <u>capacity</u>.

The potential at the inert <u>platinum electrode</u> is created by an excess or loss of electrons at the electrode surface. A reducing solution has a tendency to donate electrons and an oxidizing solution has a tendency to accept electrons.

The <u>reference electrode</u> is constructed to give a constant potential. A calomel electrode consists of mercury in contact with mercurous chloride (calomel) which, when immersed in a solution (KCl) with a constant chloride activity, maintains a stable potential. A glass body surrounds the electrode and contact with the outer solution is provided through a liquid junction. The electrode reaction may be written:

$$Hg_2Cl_{2(s)} + 2e^- \Leftrightarrow 2Hg_{(l)} + 2Cl^- \qquad \text{(VI)}$$

When redox changes occur at the electrode, the electrode potential is kept constant either by the dissolution or precipitation of Hg_2Cl_2. The silver/silver chloride electrode works on the same principles.

The nature of the redox potential

Redox reactions in natural waters and sediments very seldom reach equilibrium and are seldom reversible due to the continuous biological activity. The redox state of a natural environment is the result of a variable number of redox reactions which may proceed independently of each other. Thus, what is measured in a natural environment, is a mixed potential which is of little value for quantitative chemical calculations (Stumm, 1966). However, the redox potential gives information on the kind of chemical and biological reactions that can take place. Therefore the redox state of a sediment or water is a valuable measurement when characterising an environment for ecological purposes or in pollution research. To determine e.g. the level of the redoxcline * in a water body of a sediment is often more important than to measure the absolute value of the redox potential. (Fig. 4.1.1.)

In a recent work by Bågander and Niemistö (MS), it has been shown that it was possible to obtain reproducible results from replicate sediment cores, taken at 17 stations in the Gulf of Bothnia and the Gothland deep, using two independently designed sets of equipment for measuring redox potential.

E_h-measurements

Equipment: platinum electrode, calomel reference electrode and a potentiometric instrument, usually a pH-meter with a millivolt scale.

Commercial platinum electrodes are expensive compared to home-made electrodes. A platinum wire (e.g. 25 mm long and 0.5 mm in diameter) is fused into the end of a sodium glass tube or cemented into the end of a plastic tube. The electrode area is adjusted to a suitable size by cutting the wire or enlarging it with a platinum foil. It is thus very easy to design a platinum electrode for a special purpose. As a general rule, for greatest accuracy in measurements, the platinum electrode area should be as large as possible within the practical limits for each type of measurement. However, the effect of certain surface contaminations may increase with larger electrode area (Stumm and Morgan 1970).

Commercial calomel reference electrodes are available with either saturated or 3.5 M KCl solution as reference electrolyte. Standard potentials for the calomel

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* Redoxcline: A gradient in the redox state (Hallberg, 1972). Sometimes also called Redox Potential Discontinuity layer (RPD-layer), a somewhat unfortunate term, since no discontinuity is involved, but simply a sharp gradient.

electrode are given in Table 1. The 3.5 M KCl solution is recommended for field work. The saturated KCl solution may cause erratic potentials if KCl is precipitated on the calomel or at the liquid junction due to low temperature.

Table 1   Standard potentials of calomel electrodes (Volt) (relative to standard hydrogen electrode). From Whitfield (1971b).

Temperature $^{\circ}$C	3.5 M KCl	Saturated KCl
10	0.2556	0.2543
15	0.2538 *	0.2511
20	0.2520	0.2479
25	0.2501	0.2444

* Calculated by the present author

Calibration

The ZoBell solution (0.003 M potassium ferrocyanide, 0.003 M potassium ferricyanide in 0.1 M KCl) is most frequently used for calibrations when measuring E_h. The potential of this solution is +430 mV at 25°C (ZoBell, 1946).

Handling of electrodes

The platinum electrode surface must be kept as clean as possible. Mechanical cleaning using a mild abrasive or a tissue followed by rinsing with distilled water is a recommendable method which is practical in field work. Chemical cleaning must be used with care because the electrode surface may be damaged.

The liquid junction of the reference electrode is easily affected by suspended particles or precipitates, which may change the liquid junction potential. The reference electrode should therefore not be inserted into solutions with suspended particles or in a sediment. The use of a salt bridge between the sample and the reference electrode prevents such errors.

Stabilization of readings

Samples of natural waters and sediments are often poorly buffered with respect to redox potential. Therefore, it often takes some time to get a stable reading. Electrode drift of several hundred millivolts may occur during the first minute of measurement (Figs. 4.1.2 and 4.1.3). Stabilization usually commences within 5 to 10 minutes and an electrode drift of less than 2 mV/min can be accepted as a

good reading. Sometimes considerably larger drift can be accepted, depending on the purpose of an investigation or to avoid too long storage of the sample between sampling and the last measurements.

When introduced into a sample the redox electrode always causes some degree of disturbance. Sediment samples are most sensitive because part of the sediment structure is broken and the interstitial water is pressed away. The shape and size of the electrode must be designed to minimize these effects. Electrode drift due to introduction of air or loss of gas when the electrode penetrates the sediment must also be considered. Absolute stabilization never occurs because of the continuous biological activity.

Effect of pH

The redox potential is dependent on pH, which e.g. controls ionic equilibria, solubilities and the formation of complex ions, etc. The E_h/pH relationship is usually very complicated and a factor to correct E_h readings of natural samples for a certain pH cannot be given. An average change of about -0.061 V for each unit increase in pH, in the pH range of 3 to 10, has been reported by ZoBell (1946). However, redox measurements are not usually corrected for pH, but reported together with the pH value.

Effect of temperature

Theoretically the effect of temperature is expressed by equation (III). But in the complex natural systems this effect is as complicated to calculate as that of pH. Temperature affects e.g. solubilities, reaction rates, pH, etc. In four different marine mud samples it has been shown that a change in temperature, from 0° to 20^oC, caused a change in E_h between 0.01 to 0.02 volts (ZoBell 1946).

Reproducibility of E_h measurements

The redox capacity of a system is responsible for the reproducibility of the E_h measurements. Natural systems often have a low redox capacity, therefore E_h measurements seldom can be reproduced to an accuracy greater than ± 0.01 volts. A sediment, though appearing homogeneous, contains microenvironments where the redox potential is affected by microbiological activity. Therefore, parallel readings may differ by as much as ± 0.05 volts or even more.

Sampling of sediment for E_h measurements

In situ E_h measurements are most accurate because the natural environment is more or less changed by any sampling technique. In situ probes for E_h and pH measurements have been constructed and used by e.g. Manheim (1961) and Whitfield (1971 a). In situ probes are used for profiling in the water column and the uppermost few centimetres of the sediment. However, E_h in water and sediment is generally measured in samples. It has to be stressed that the term "undisturbed" often used in connection with sediment samples is misleading since no sediment sampler ever constructed is capable of taking undisturbed samples. When dealing with E_h measurements and chemistry of the sediment it is necessary that the measured parameters can be related to a certain level of the sediment. A sediment corer is the only type of sampler that will give satisfactory sediment samples for that purpose. The corer must be designed and used in such a way that the shock wave in front of the corer is minimized. Otherwise the surface layer of the sediment, which is often very soft, will be swept away. Sediment cores taken by a diver are by all means superior to any other sampling technique.

Different techniques can be used for redox measurements in a sediment core e.g.:

1. An E_h electrode long enough to be introduced continuously or stepwise into the sediment core
2. A coring tube with apertures at certain levels where the electrode can be inserted
3. Sectioning of the sediment core into subsample slices, which must be protected from contact with the air during both the storing and the measuring procedure.

A complete system including sampling, subsampling by sectioning, and storing of the sediment, especially useful for redox measurements, has been designed and described by Niemistö, 1974.

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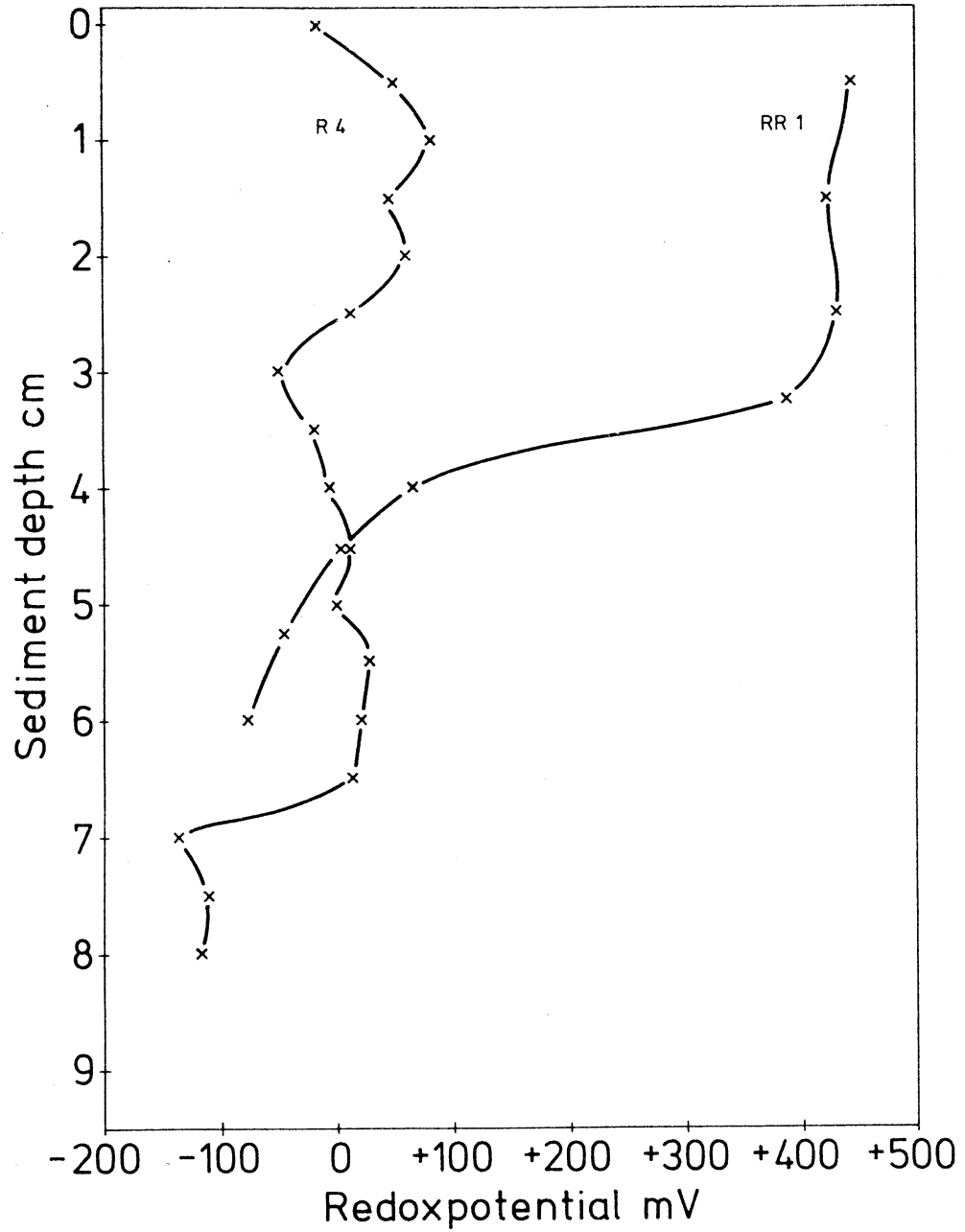ZOBELL, C.E. 1946. Studies on redox potential of marine sediments. - Bull. Am. Assoc. Petrol. Geol., 30:477-513.

Fig. 4:1.1 E_h profiles from two sediment cores. In core RR 1 a distinct redox-
cline is situated at the 3.5 cm level. In core R 4 the redoxcline is
situated in the water above and the sediment is reduced from the top
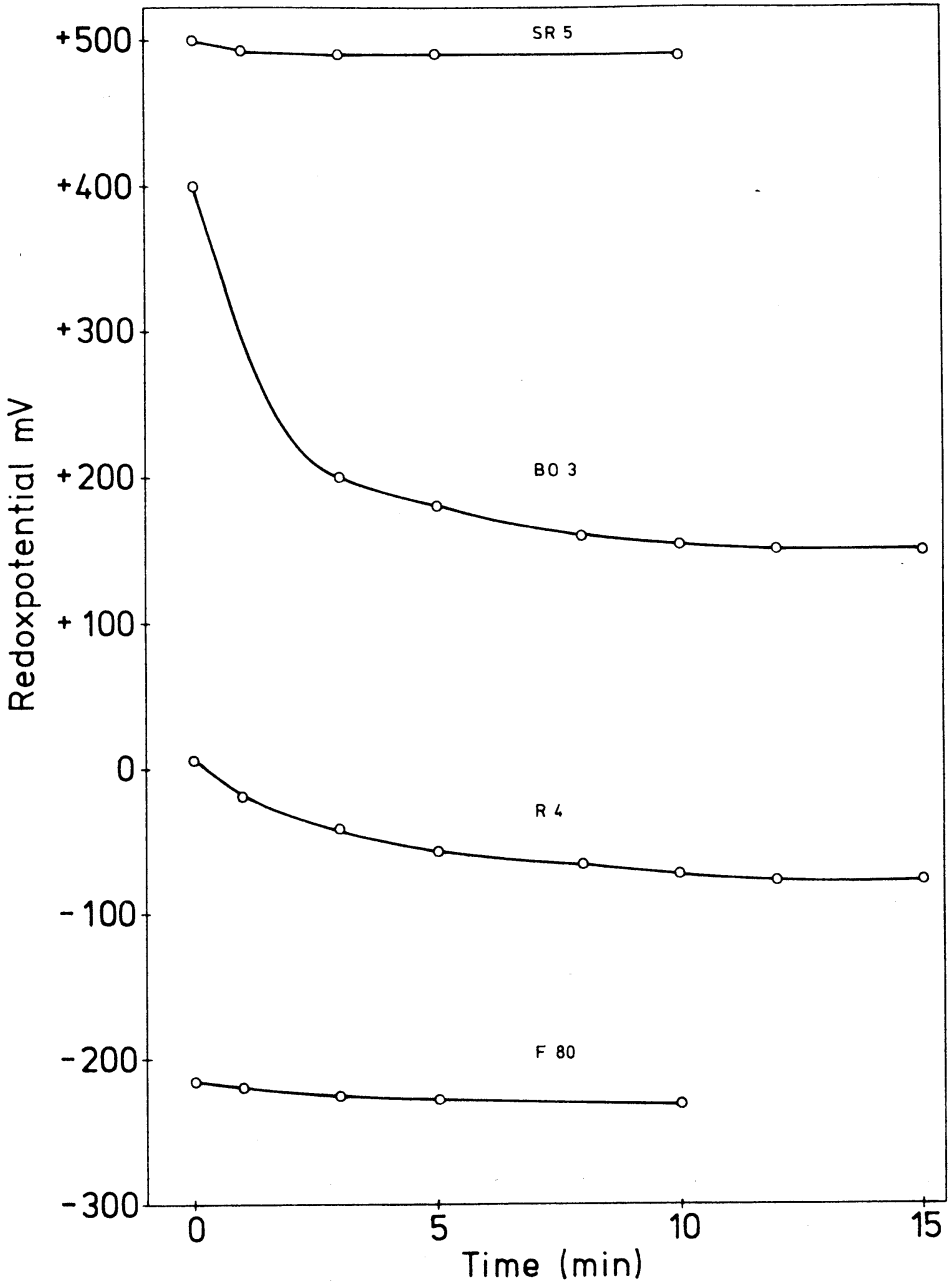layer.

Fig. 4:1.2 Electrode drift in four sediment samples at different redox states. Intermediate redox values around the redoxcline (BO 3) are stabilized more slowly due to the unstable redox situation.
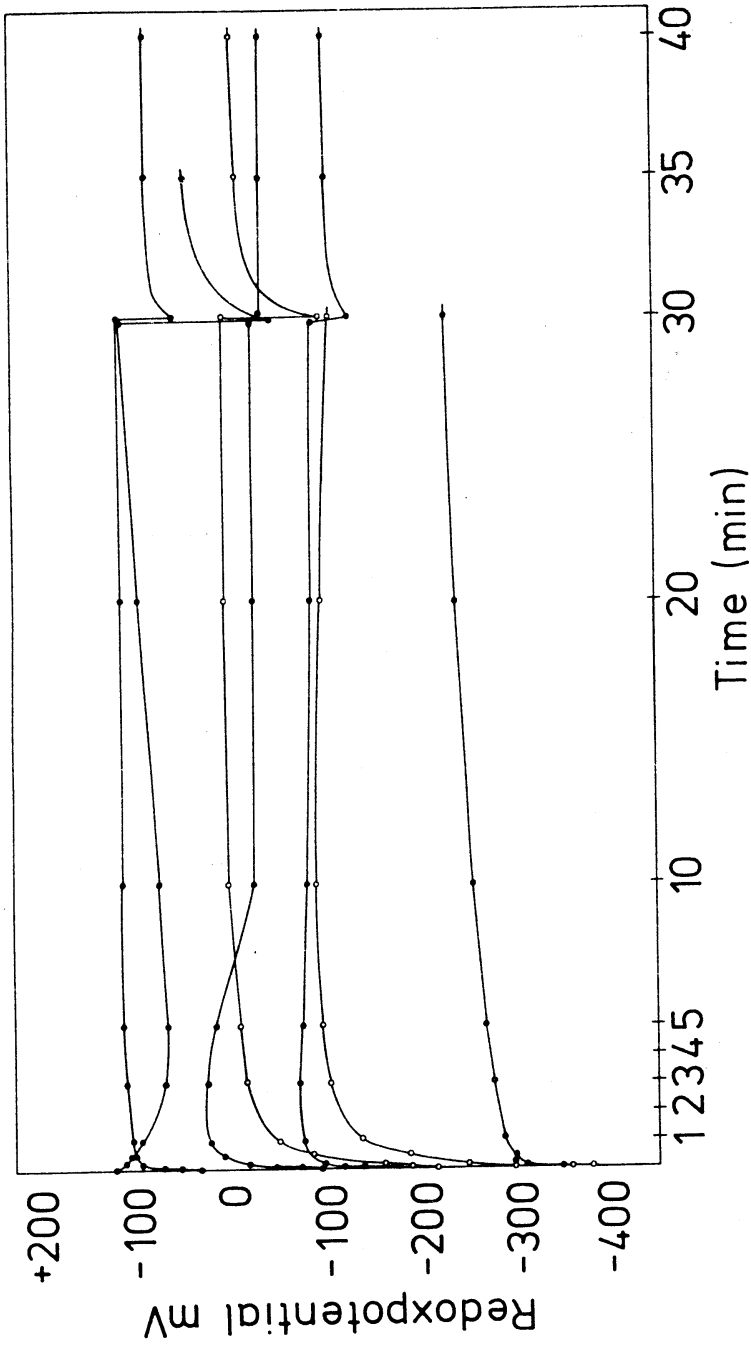
Fig. 4:1.3   Electrode drift of seven in situ measurements made on a Dutch tidal flat sediment. After 30 minutes the electrode was withdrawn 5-10 mm. Stabilization will thereafter be attained at lower values. (Modified from Hallberg 1968).