

EH-MEASUREMENTS IN MARINE SEDIMENTS UNDER LABORATORY CONDITIONS (1).

by

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Résumé

Mesures du Eh des sédiments marins au laboratoire

Des expériences ont été entreprises au laboratoire sur des sédiments marins. Des échantillons de sable en provenance de différentes plages du Nord de l'Adriatique étaient placés dans des tubes de plastique transparent. Il faut à peu près quatre semaines pour que le potentiel d'oxydo-réduction retrouve sa répartition « naturelle ». Des électrodes de platine et d'or, placées dans le sable à différentes profondeurs, permettent d'obtenir des mesures continues du potentiel d'oxydo-réduction. Après quelques jours, on atteint des valeurs stables et constantes. Le nettoyage mécanique et la remise en place des électrodes affectent, dans une certaine mesure, les valeurs des potentiels qui se trouvent être proches du point du système où le potentiel, réellement mesuré entre l'électrode au calomel et l'électrode de métal, est égal à 0. Après quelques jours, les mesures avaient de nouveau atteint les valeurs enregistrées avant le nettoyage.

Introduction

Since Zobell's (1946) work on redox potentials in marine sediments, the subject has become of great interest, not only to geologists, but also to biologists. Whitfield (1969) thoroughly discusses the fundamentals of Eh" measurements and associated problems. The methods most frequently employed for measuring redox potentials are: introduction of one or more electrodes into the sediment layer of interest; extraction of a sediment sample with a tube and insertion of electrodes through prefabricated holes from the side of the tube (Riedl and Ott, 1970) and laboratory experiments. Most of the results, obtained with the first two methods outlined above, share the fact that measurements lasted only for a comparatively short period of time, usually only until a seemingly stable reading was reached. In the laboratory, on the other hand, long term measurements under controlled conditions can easily be carried out.

(1) Financial support was provided by Deutsche Forschungsgemeinschaft (DFG) and Fonds zur Förderung der wissenschaftlichen Forschung in Österreich. We thank A. Bleichner for drawing the figures.

Material and methods

Fig. 1 shows a setup well suited for long-term measurements in marine sediments. The central unit consists of two plexiglass tubes (D), which can be closed on both ends by a lid. Through conical drillholes sealed with silicone rubber on the side of the tubes, electrodes may be inserted into the sediment at various depths from the sand surface. From reservoirs (A),

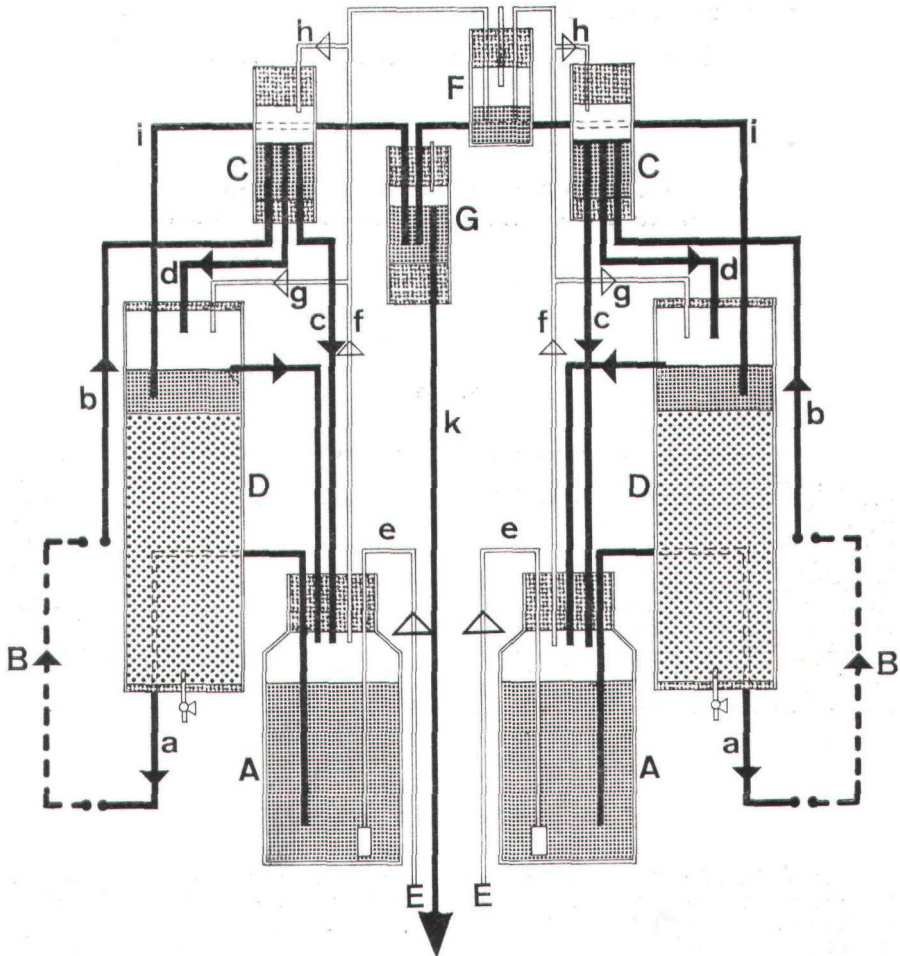


FIG. 1.

Schematic flow diagram of the setup used for Eh monitoring. One half of the symmetrical unit can be used as control.

For detailed explanation, see text.

water is pumped by pumps (B) through the pipes (a) and (b) into containers (C). From C, water flows via d over the sand surface and back to A or directly back to A through C, thereby establishing a controllable hydrostatic head between C and D in order to keep the flow across D constant. Air or other gases may be pumped from input (E) through pipes (e) into reservoirs (A). Connections (f, g, h) provide a path for pressure equa-

lization between the air-tight containers. Excess gas is allowed to escape in F against an adjustable hydrostatic head so that the pressure inside the system can be kept slightly above ambient. Salt bridges (i) electrically link the sand columns to a common container (G) which houses the reference electrode. G is mounted below the waterlevels in D such that a constant slow outflow provides chemical decoupling. This water leaves the system through k. Water and gas flow can be regulated on all connecting units. Also, water can be drained through the bottom of the sediment columns. The entire apparatus consists of two separate systems set up symmetrically to allow for control measurements. Holes were made into the lids of the central units (D) to control temperature and pH. Both parameters were kept constant during the experiments.

The sand used in the experiments was taken mainly from a small beach in Strunjan near Portoroz, Jugoslavia. Some experiments were conducted using sediment from the Lido in Venice, Italy, for comparison. For measuring electrode potentials (Fig. 2), a high impedance voltmeter

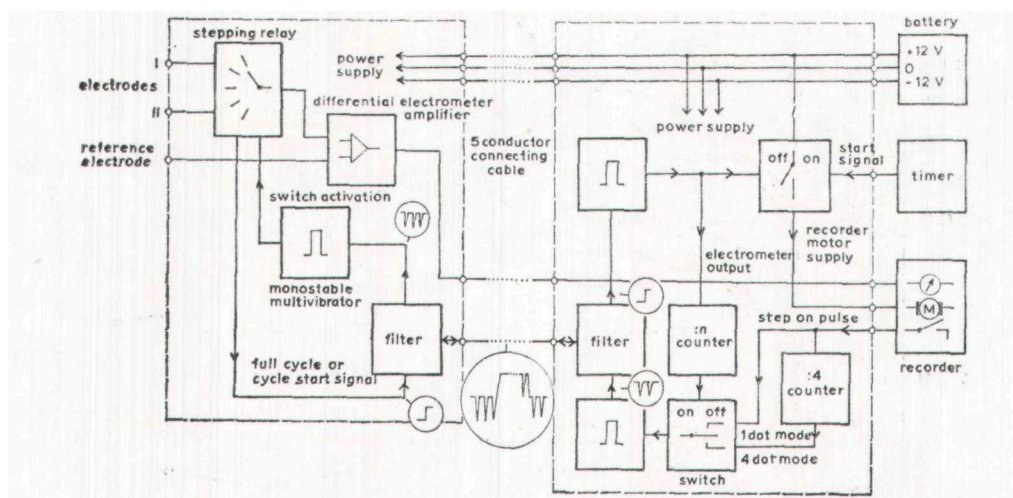


FIG. 2.

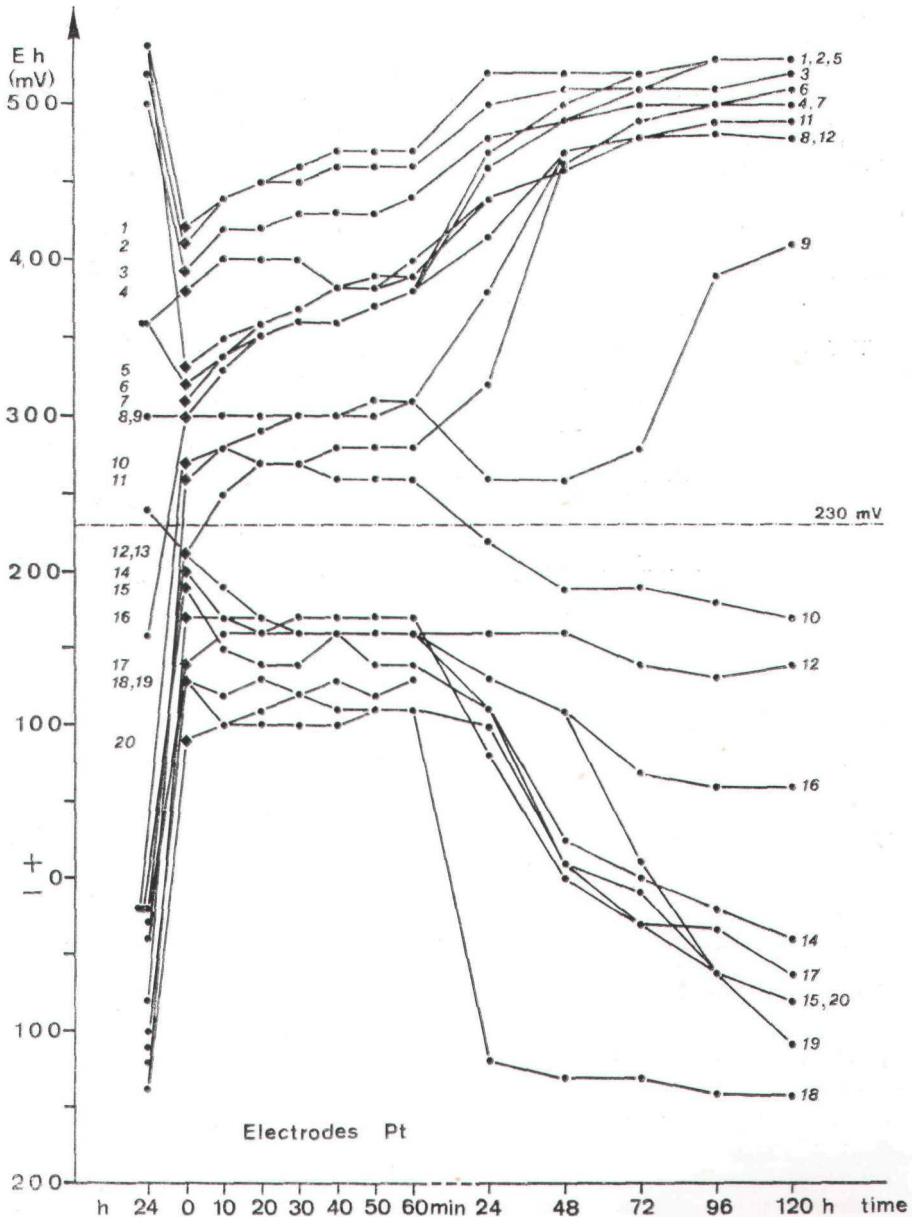
Block diagram of the electronic circuit. Arrows indicate direction of signal flow. Signal display in circles (According to Machan and Ott, 1972).

or electrometer is needed. Current flow must be kept essentially zero. We used an electrometer amplifier with differential input so that the potential of the columns could be left floating within certain limits.

A 12-position stepping relay was connected between amplifier input and metal electrodes. By energizing the relay synchronously with the falling bar of the recorder, we got 12 distinct tracks on the chart. Specific interruptions in the tracks were used for labelling during automatic operation. A more detailed description of the electronic circuit is given in Machan and Ott (1972).

We conducted the majority of our experiments on sediment columns which has been standing in the laboratory for a considerable period of time and in which the redox system had stabilized. Stabilization, in the sense used in this report, means that the redox-potential-discontinuity has reached a stable position in the sediment, presumably corresponding to natural conditions. The term will be restricted to the sediment alone, not including any measuring device. Measurements of the redox potential, started immediately after filling the columns, do not allow to distinguish whether a change in the reading is a consequence of changes in the sand system or if the

chemical and biological activity is influencing the electrode itself. A series of experiments was carried out in order to differentiate between actual Eh-fluctuations and those simulated by the technical procedure. Both may produce similar changes in the recorded potential. The terms "Eh value" and "measured potential" should therefore not be confused. But, as we have no knowledge of the true Eh value, the



Changes in measured potential as a function of time during an experiment. Numbers at left side correspond to electrodes at black squares. Numbers on right side relate electrodes to end-points of curves. Electrodes were cleaned at time zero. The time scale is not linear. Platinum electrodes.

measured electrode potential is often called Eh for simplicity. One method to determine simulated Eh-changes simply consists in removing the electrodes from the sediment, cleaning them mechanically and reinserting them and recording the potentials. This technique was performed in the following experiments.

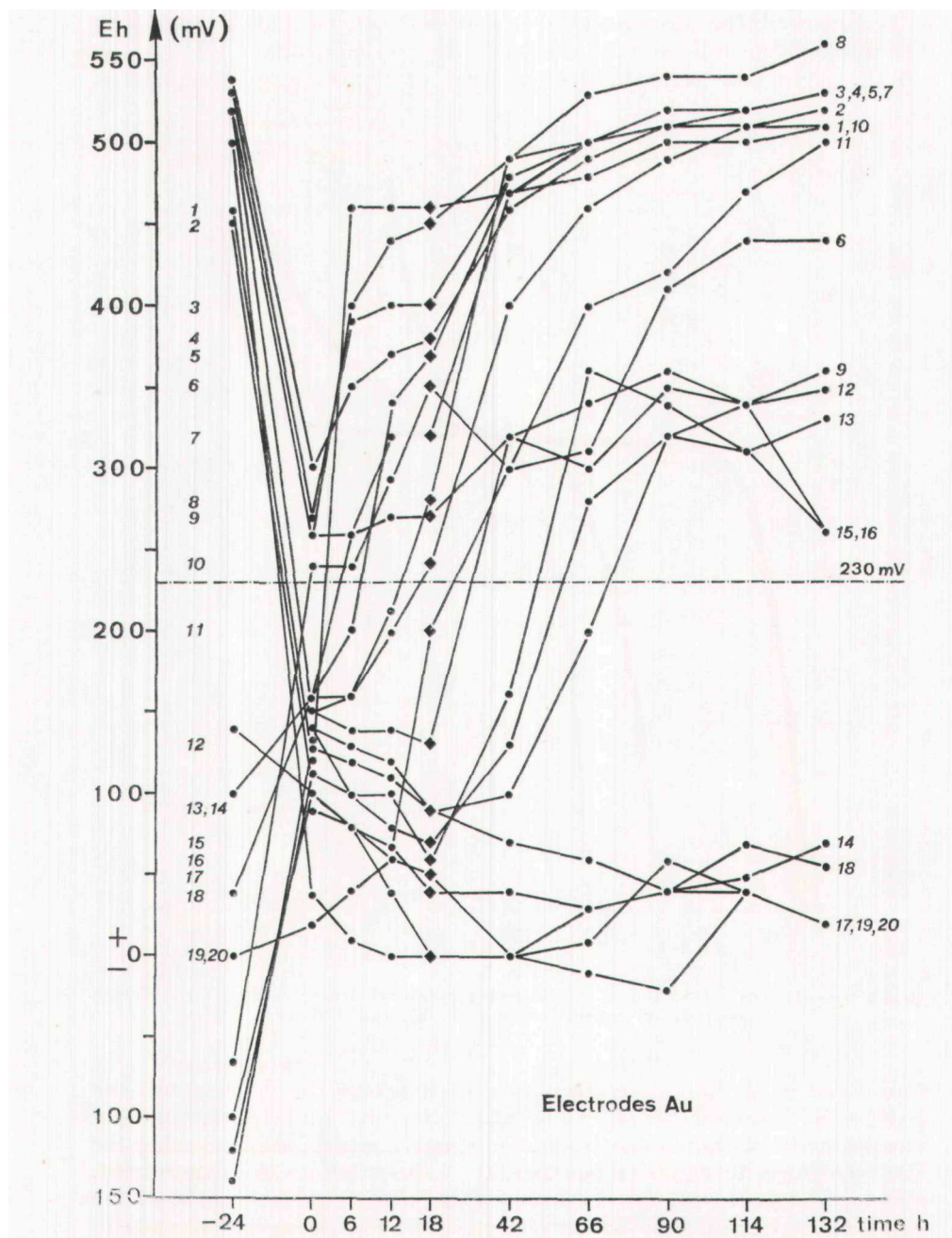


FIG. 4.

Same as Fig. 2, but for gold electrodes.

Results

Fig. 3 and 4 show the recorded potentials of twenty electrodes as a function of time. Both platinum (Pt) and gold (Au) electrodes were used, major differences between these metals were not found in these experiments. The electrodes are numbered (Fig. 3 and 4) such that the numbers on the left side designate the square symbols while those on the right side refer to the endpoint of the corresponding curve.

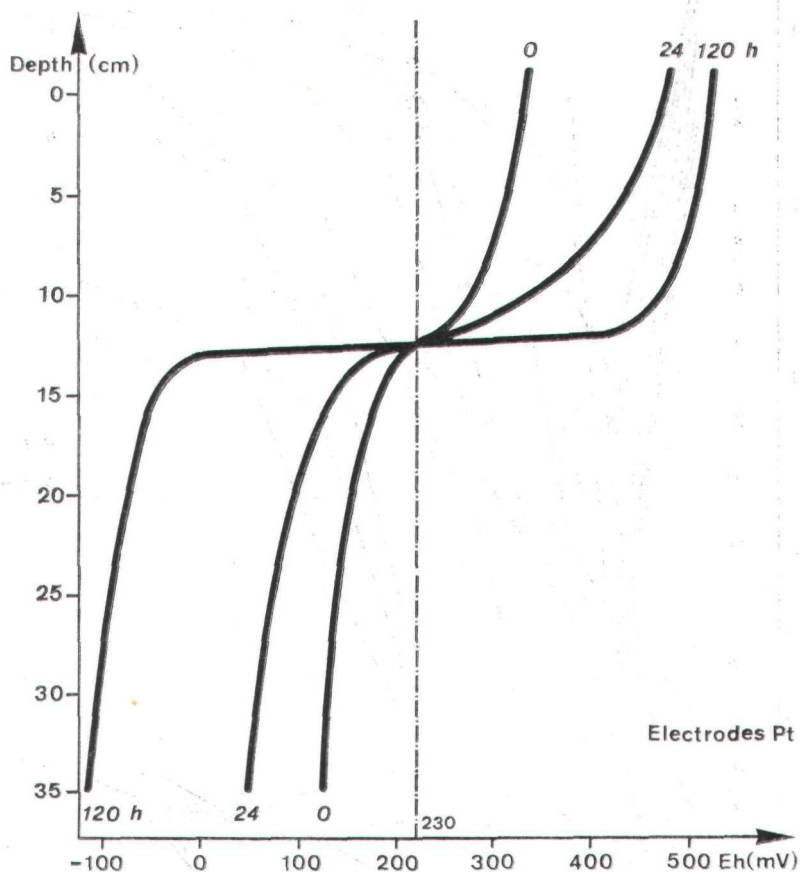


FIG. 6.

Redox potential as a function of depth (redox potential discontinuity) for different periods of reequilibration (0, 24 and 120 h).

Compared with the values measured 24 h before the experiment, the potentials observed immediately after cleaning and reinserting the electrodes lie within a much smaller range. Some time is needed for the recordings to reach values similar to those before the experiment. Only a few electrodes do not follow this pattern, probably due to the experimental conditions which allow H_2S to escape and/or oxygen to enter the system, thereby producing higher readings. Changes in the slope of the curves shown are caused by the nonlinear time scale.

The fact that reproducible results could be obtained in all but two or three cases, is an indication that a stable condition in the columns had been reached. The process usually took up four weeks. Filling and transporting the columns to Vienna added to the mixing of the originally established layers but, even in the natural biotope, there is considerable mixing of the sediment. Fig. 5 and 6 show the recorded potentials as a function of depth for the Pt- and Au-electrodes. The inner curve (relative to the dotted line) was measured immediately after inserting the electrodes, the second curves 24 and

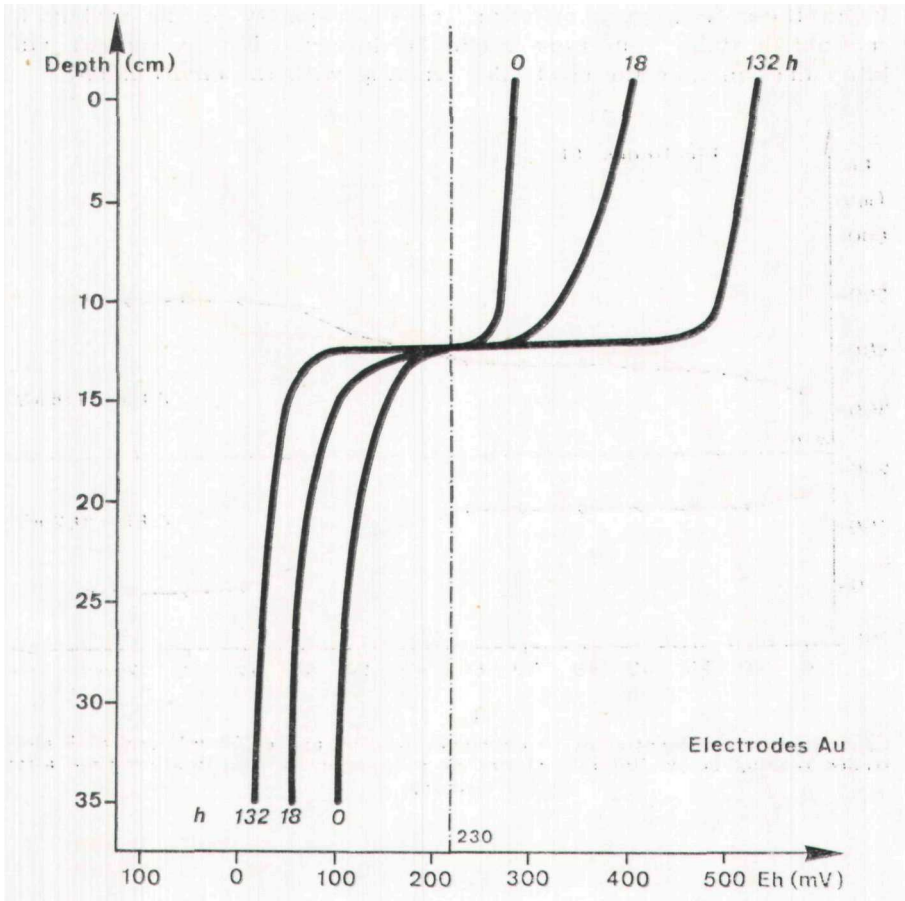


FIG. 6.

Same as Fig. 5, but for gold electrodes (0, 18 and 132 h).

18 h later, respectively, and the third curves 120 and 132 h later. The shift in the potential is quite obvious.

Another effect is noticeable in Fig. 3 and 4: the potentials, measured immediately after reinserting the electrode, lie close to the "zero point" of the system, 230 mV, where the actually measured potential between calomel electrode and metal electrode is 0. This means that the system by itself only measures its own zero. The deviation from the zero point, which could theoretically be reached,

is determined by the environment, that is the actual Eh. It clearly follows that the values, read immediately after the insertion of the electrodes, correspond to the actual conditions. In Fig. 7, the data for electrodes 10 and 8, respectively, were pooled, producing a curve for the potentials above the zero line and one for those below the zero line which conform to positive and negative Eh values. It can be seen, in both cases, that the measured potentials depart from system zero (230 mV) to return to their original values. It is surprising that even the relative deviation in the positive and negative direction is approximately equal at the end of the five days (174 and 162 mV). From these findings a criterion for the capacity of the system to reestablish stable conditions might be derived. In this context, stability does include the electrodes reacting with the environment.

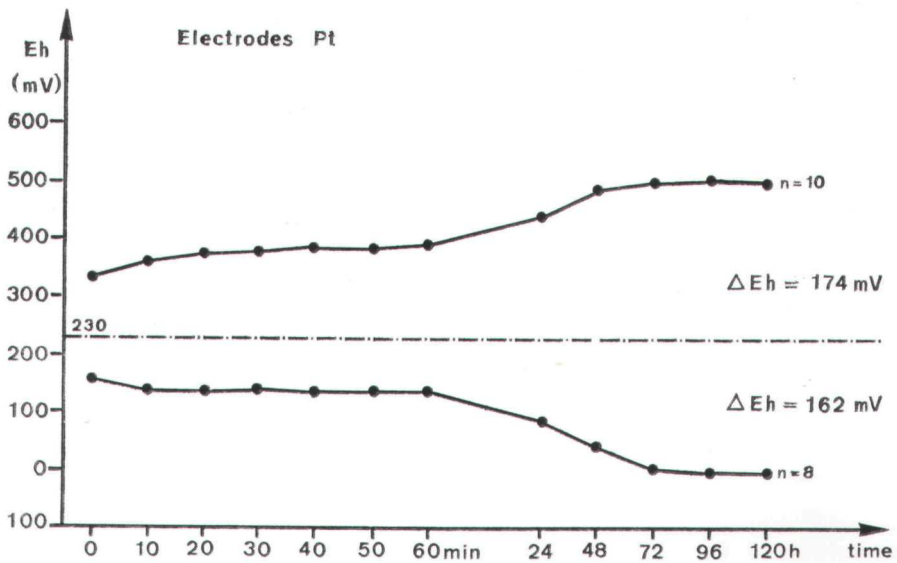


FIG. 7.

Calculated mean potential of 10 electrodes reading above 230 mV and of 8 electrodes reading below 230 mV, shown as a function of equilibration time after cleaning.

Discussion

The process of reequilibration has been mentioned in Machan and Ott (1972). They found that the time needed could be quite variable but had no control of the conditions prior to the insertion of the probe. The quality of the sediment probably influences the time needed significantly. No statement can be made on this problem because the sands we took at three different locations in the northern Adriatic were quite similar in this respect. Mechanical disturbance by the electrode and electrochemical influence in their vicinity might again be important factors. But how these factors combine to yield the measured results can not yet be quantitatively stated.

Summary

Experiments with marine sediments were made under laboratory conditions. Sand samples, taken from different beaches in the northern Adriatic Sea, were filled into columns of plexiglass. It took about four weeks for the redox potential to reassume its « natural » distribution. Electrodes of platinum and gold were inserted in different depths from the sand surface and the redox potentials recorded continuously. After some days, stable and constant values were reached. Mechanically cleaning and reinserting the electrodes significantly changed the measured potentials. They lie close to the point of the system where the actually measured potential between the calomel electrode and the metal electrode is 0. After some days, the readings had again returned to the values recorded before cleaning.

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