

# Polarographic characterisation of some trace elements in sea water

by

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## Introduction

The experimental characterization of the actual ionic states of trace elements in sea water is a very important and complex problem. The concentration level of trace elements is so low that the distinction of various complex species, and sometimes even their detection by conventional physico-chemical methods, is impossible. Some of the polarographic techniques, such as squarewave (s.-w.), pulse-, radio- and anodic stripping polarography, appeared to be useful for the determination of the concentrations of trace elements in sea water. The application of polarography to the determination of the actual ionic states of added or naturally occurring microconstituents in sea water, and to their interaction with added chelating agents seems to be very promising.

## Analytical characterization

Classical d.c. polarography enables the determination of elements in concentrations down to a few micrograms per milliliter. However, the concentrations of trace elements in sea water are about one thousand times lower (Rep. 1964). The recently developed high sensitivity polarographic techniques can be applied to the direct determination of some trace elements in sea water.

Some of the important improvements in the polarographic determination of trace elements in sea water are proper deaeration and pre-electrolysis. By deaerating sea water, it becomes more alkaline because of the removal of CO<sub>2</sub>. This effect can be overcome by passing an inert gas through a solution having the correct salt concentration and carbonate-bicarbonate ratio. Potentiostatically pre-electrolysed sea water, enables the evaluation of the corresponding calibration line to a lower concentration range than that of the analyzed trace element present in untreated natural sea water. The accuracy of trace determination, at maximum instrument sensitivities, can be improved by statistical treatment of the results obtained by the standard addition method.

The pulse polarographic technique appeared to be very useful for the determination of trace element concentrations of about 10<sup>-8</sup> M. In our laboratory, this technique was used for direct determination of zinc and iodate in sea water [PETEK & BRANICA to be published]. This method could possibly also be used in the determination of some other trace elements in sea water.

Anodic stripping polarography is nowadays the most promising technique in the determination of trace element concentrations in sea water. MACCHI [1965] used the dropping mercury electrode with a very long drop time ( $t = 68$  sec.) for the determination of ionic zinc in sea water. Whitnack (private communication) used the hanging mercury drop (on Pt-Au wire) as the working electrode.

For the determination of zinc (Fig. 1) we used the hanging mercury drop electrode according to KEMULA & KUBLIC [1963].

## Physico-chemical characterization

The physico-chemical state of microconstituents in sea water plays a very important role in processes of their fixation in sediments as well as in the uptake into marine biota.

*Rapp. Comm. int. Mer Médit.*, **19**, 5, pp. 929-933, 2 fig. (1969).

The ionic states of trace elements in aqueous solution can be determined by using classical polarography [CROW & WESTWOOD, 1965 and HEYROVSKY & KUNTA, 1965]. The complexibility of metals can be evaluated from the shifts in their reversible polarographic half-wave potentials [DE FORD & HUME, 1951] and or from the ratios of their limiting currents in the case of frozen chemical reactions [ACKERMAN SCHWARZENBACH, 1952, and SCHWARZENBACH & GUT, 1956]. However, the rates of the chemical reactions are not often slow enough, so that the kinetic parameters should be taken into account [KORYTA, 1959 and 1962]. The element studied, therefore, should be added to the sea water, since their original concentrations are too low. In order to avoid this addition, however, and be closer to the conditions present in natural sea water, the amalgam, pulse and square-wave polarographic techniques can be applied.

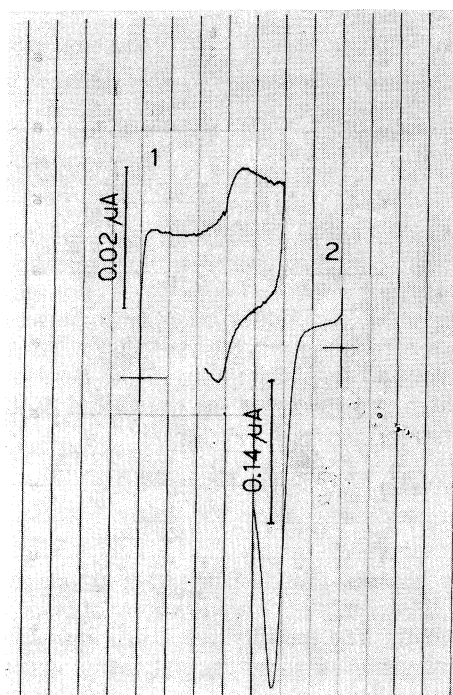


FIG. 1. — Voltammetric curves of Zn naturally occurring in sea water, recorded with hanging mercury drop electrode (scan rate 0.8 V/min.)  
 1. Cyclic voltammogram curve  
 2. Anodic dissolution after 4 minutes pre-electrolysis with stirring on -1.2V vs. S.C.E.

#### *Amalgam polarography*

We used the dropping amalgam electrode for the determination of the half-wave potentials of zinc, cadmium and indium amalgam oxidation [Ann. Rep. 1965-1966]. The complexation with chloride ion and the hydrolysis of the mentioned metals was investigated by the shifts in their half-wave potentials. The obtained results show that ionic zinc is present in sea water (at pH = 8.3) in the form of  $ZnOH^+$  and  $Zn^{++}$ , each 50 per 100 and that ionic cadmium is predominantly in the form of  $CdCl^+$  [BARIC & BRANICA, 1967]. Preliminary results showed that indium ions are hydrolyzed and at the same time interact with chloride ions.

#### *Square-wave polarography*

According to MATSUDA's [1958] equations the s.-w. peak height depends strongly on the degree of reversibility or on the symmetry of the electrode reaction. The rate of the electrochemical reaction is correlated with the ionic state of the depolarizer. This method was proved successful in our laboratory for uranyl [JEFTIĆ & BRANICA, 1963], copper [PETEK *et al.*, 1964] and indium [ĆOSOVIĆ & BRANICA, 1966] acetylacetonates, and probably it could be also applied to the characterization of the ionic forms even at very low concentrations (down to  $5 \times 10^{-8}M$ ).

The influence of the surface active agents on the s.w. peak height is sometimes specific for different ionic species reduced [JEFTIĆ & BRANICA, 1963]. By the above mentioned methods, the stability constants of the metallic complex formed can be evaluated.

### *Pulse polarography*

Using pulse polarography, the ionic state of microconstituents can be proposed from the logarithmic plots of the « normal polarograms » [CHRISTIE *et al.*, 1966]. From the measured peak current of « derivative polarograms », the rate of the electrode reaction can be determined. From these data, a conclusion as to the ionic form of the electroactive species can be deduced.

### *Chelation of metals*

By adding EDTA, several authors tried to obtain an explanation as to the effect of the ionic state of microconstituents in the uptake and fixation processes. However, the experimental evidence for the interaction between the investigated microconstituents and EDTA in sea water has not been given.

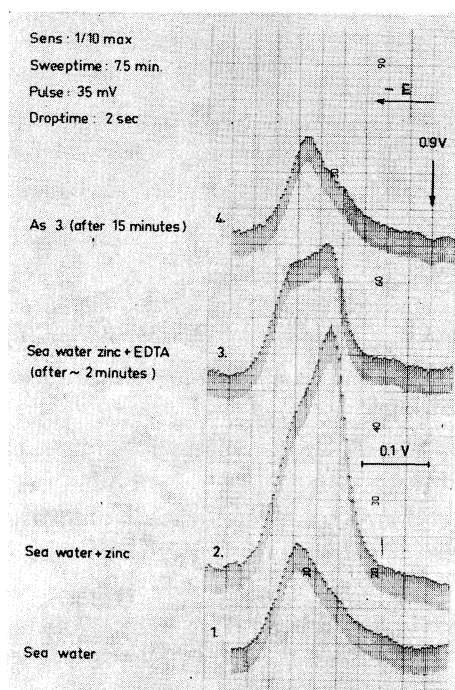


FIG. 2. — The influence of EDTA on the pulse polarographic peak height of zinc in sea water. Polarograms of sea water (curve 1), sea water with zinc added (curve 2), the same sample with EDTA added (curve 3), and the same sample recorded after 15 minutes. Record conditions: voltage sweep 7.5 min., delay time 2 sec.; derivative, pulse height 35 mV; integration 3 drop lives; 1/10 maximum sensitivity; Southern Harwell Pulse Polarograph Mark II.

Using the pulse polarography, our experiments show that there is an interaction between zinc and EDTA added to sea water (Fig. 2). At given conditions, the whole zinc present was bound to EDTA after 15 minutes [Ann. Rep., 1965-1966]. The studies on Cd - EDTA reactions in sea water by square-wave polarography show that this complexation is also a time consuming process [MALJKOVIĆ, 1967].

### Conclusion

Some polarographic techniques can be used successfully for the characterization of microconstituents in sea water :

- (i) for a quantitative determination
- (ii) for the determination of the ionic state, complex stability and reaction kinetics (homogeneous and heterogeneous).
- (iii) for chelation of metals with ligands added to sea water.

The main advantage of polarography in comparison with other methods used so far is its high sensitivity which enables the study of sea water at fairly natural conditions.

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