ELECTROCHEMICAL REDUCTION OF

o-NITROPHENOL AS A TOOL FOR THE ROUGH CHARACTERIZATION OF

ORGANIC MATTER IN SEAWATER SAMPLES

Bla`enka GA[PAROVI] and Bo`ena]OSOVI]

Center for Marine Research Zagreb, Ru|er Bo{kovi} Institute,
PO Box 1016, 41001 Zagreb, CROATIA

ABSTRACT

Phase sensitive alternating current (a.c.) voltammetry with o-nitrophenol (ONP) as a probe is used as a simple nondestructive method for a rough characterization of organic substances in natural seawater samples. This is based on the measurement of the effects of adsorbed organic substances on the peak height and the potential of the ONP reduction peak. In this work is presented further improvement of the method which is achieved by introducing the measurement of the prepeak of ONP reduction obtained upon scan reversal. The height of the prepeak is extremely sensitive upon the type of organic matter adsorbed on the mercury electrode at the pH of natural seawater. The ONP prepeak increases in the presence of adsorbed layers of negatively charged organic substances, such as humic and fulvic acids and proteins. In the presence of adsorbed polysaccharides of dextran type there is no increase of the ONP prepeak height or even a small decrease of the prepeak is observed with the increasing concentration of the polysaccharides.

The application of the method is demonstrated on different seawater samples from the north Adriatic sea.

KEY WORDS: Organic matter in seawater, o-nitrophenol reduction

INTRODUCTION

Naturally occurring organic matter represents a complex mixture, not enough investigated so far (80 % of all dissolved organic matter species is not characterized), composed of a great variety of compounds which undergo different reactions (physical, chemical and/or biological) leading to the formation of inorganic or new organic matter [1]. Organic matter is present in the water column in the dissolved, colloidal and

particulate states with the dissolved state as the main part of it [2]. The sources of the dissolved organic matter in the sea are the products of the bacterial decomposition and autolysis of plants and animals, their metabolic excretions, with the in-situ production of planctonic organisms as a main source [3], as well as organic matter supplied from the land, which is arround 10%. Using fluorescence as a method for studying dissolved organic carbon (DOC) components it was found that protein-type components were dominant in the upper water column, while humic-type components were dominant in the deeper samples of sea [4]. For the sea surface it was found that the spontaneously formed surface films are mostly composed of glycoproteins and proteoglycans which are probably of biological exudate origin [5].

Dissolved organic matter exerts a significant influence on the chemistry of the waters specially including processes on the phase boundaries. Namely, as a large part of organic matter possesses surface active properties they tend to accumulate to phase boundaries influencing mass and energy transfer through them [6]. These processes can be simulated at the model electrode/water interface using different electrochemical methods.

Alternating current voltammetry, in phase and out of phase measurements, are nondestructive direct analytical techniques suitable for investigation of adsorbable organic substances in aquatic systems, particularly in natural water samples [7,8]. Many of the organic compounds of both natural (e.g. fulvic and humic acids, and extracelular metabolites of algae) and anthropogenic (e.g. detergents) origins present in waters have a surface active effect on the mercury electrode. Methods which have been used to determine these compounds in natural waters generally make use of their capacitance reducing effect. The capacitance of the electrical double layer drops when electrolyte ions and water molecules are replaced by adsorbable organic solutes. This effect can be measured at the hanging mercury drop electrode using a.c. voltammetry (out of phase). Since the surface-active effect has little specificity, additional efforts are needed to provide a rough characterisation of the complex mixture of organic

substances. Very useful additional information on the adsorption behavior of the mixture and the structure of the adsorbed layer can be obtained by investigation of the influence of the adsorbed layer on the electrode processes of other ions and molecules, which are used as a probe. Using o-nitrophenol (ONP) as an electrochemical probe a new method was proposed for the examination of organic matter composition of natural waters [9]. Namely, ac voltammetric characteristics (in phase measurements) of the ONP probe (peak height, peak potential and peak shape) are changing in different ways depending on physico-chemical properties of present organic substances in seawater samples while adsorbed on the mercury electrode.

In this work we report on further improvement of the electrochemical method using ONP probe for the rough characterization of the composition of organic matter of the natural waters. All investigations were performed in seawater samples collected in the north Adriatic sea. Results are compared with the DOC values of the investigated samples.

EXPERIMENTAL

Phase sensitive ac voltammetric measurements were performed by the EDT-ECP 110 Modular Research Polarograph (London, England). All experiments were performed in a three electrode system with hanging mercury drop electrode (HMDE) by Metrohm (Switzerland). Ag/AgCl electrode was used as the reference electrode and a platinum wire as the auxiliary electrode.

For the study of the oxidation-reduction processes of the ONP without and in the presence of organic matter with surface active properties, phase sensitive ac voltammetry (in phase mode) was used. The frequency of the ac voltage was 170 Hz, and the p-p amplitude 10 mV. Scan rate was 20 mV s^{-1}. Organic substances were

accumulated on the HMDE at the potential of -0.35 V, prior to the potential scan. Accumulation of the organic matter was performed by stirring the solution for different time periods. All solutions contained 10^{-4} M ONP either in natural seawater or in electrolyte simulating seawater conditions (0.5 M NaCl, 2×10^{-3} M NaHCO$_3$, pH 8.4), with the addition of increasing concentrations of investigated organic substances.

The study of adsorption of selected organic substances was performed under the same conditions as above except for the phase angle which was 90° out of phase with the applied voltage. The resulting capacitive current was used for the construction of adsorption isotherms.

ONP and albumine (egg) (Sigma Chemical Co., USA), dextrane (average mol wt. 70000, Serva, Germany), and linoleic acid (Fluka, Switzerland) were used without further purification. Humic and fulvic acids provided from University of Perpignan, France where isolated from lagoon sediment. NaCl and NaHCO$_3$ (Kemika, Croatia) were used with prior purification with charcoal. Mercury is purified by double destilation under reduced pressure. All solutions were prepared with deionised water obtained with Milly-Q Water System (Millipore, Switzerland). Carbonate buffer was used to maintain pH 8.4. All solutions were purged with pure nitrogen for 10 min prior to voltammetric measurements. After deaeration a blanket of nitrogen was kept over the solution.

Seawater samples were collected at selected stations in the north Adriatic sea at 0.5 m, 5 m and 30 m depths in May and June 1994.

Seawater samples were measured without any previous treatment, except addition of ONP just before the experiment. The procedure is the same as with the model systems.

All seawater samples were measured without prior accumulation and with accumulation of 1, 3 and 10 min, at the potential E= -0.35 V vs Ag/AgCl electrode. Time periods of accumulation for seawater samples are chosen experimentally as most

convenient. Shorter time periods of accumulation do not supply enough material to the electrode surface while with longer adsorption times the electrode surface becomes completely covered with surface active substances, what is not suitable for the determination of concentration of organic substances.

Determination of dissolved organic carbon was carried out by DOC analyzer Shimadzu TOC 500 provided with Shimadzu High Sensitivity TOC Catalyst (Japan).

RESULTS AND DISCUSSION
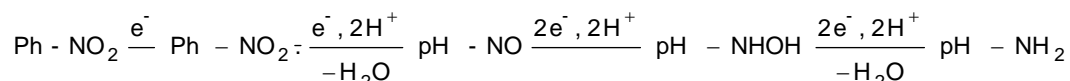
1. Model System

With the aim to find out a simple method for rough characterization of chemical composition of organic matter in natural waters we have studied ac voltammetric characteristics of ONP in the presence of different types of organic substances (humic and fulvic acis, polysaccharide, protein and unsaturated fatty acid) representative of organic matter in natural waters.

With increasing concentration of surface active substances i.e. with increasing surface coverage of the electrode by an adsorbed layer, the ac voltammetric peak of ONP on the modified electrode surface is generally decreased and shifted towards more negative potentials. At the completely covered surface the peak height and the peak potential of the ONP reduction peak become constant values characteristic for the type of adsorbed material. Estimation of the dominant type and approximate concentrations of organic substances present in different seawater samples is made by comparison of the effects of these samples on the reduction peak of ONP with those obtained with model substances.

The application of the method was demonstrated on seawater samples from the Adriatic sea [9].

In the previous paper it was hard to distinguish the effects of polysaccharides and fulvic material on the main voltammetric peak of ONP. Our intention was to improve the electrochemical method in such way that the used probe responds in a more specific way particularly to these substances.

Simple scheme of the reduction of the ONP can be described as follows

$$\text{Ph-NO}_2 \xrightarrow{\text{e}^-} \text{Ph}-\text{NO}_2^{\cdot-} \xrightarrow[-\text{H}_2\text{O}]{\text{e}^-,\,2\text{H}^+} \text{pH} - \text{NO} \xrightarrow{2\text{e}^-,\,2\text{H}^+} \text{pH} - \text{NHOH} \xrightarrow[-\text{H}_2\text{O}]{2\text{e}^-,\,2\text{H}^+} \text{pH} - \text{NH}_2$$

??????? ispravi shemu

This scheme is really more complicated owing to reactions of protonation and dismutation [10,11]. The pK value of ONP is 7.08 [12].

At the used ac voltammetric measurements overall process of reduction of ONP is irreversible. Repeating the scan at the same mercury electrode surface reversible ac voltammetric peak appears at the potential more positive than the original ONP peak.

(Figure 1)

The prepeak was recorded in the second scan at the same mercury drop (A prepeak) as well as in the third scan on the same drop after 30 s waiting at the potential E=-0.35 V (B prepeak). Generally in the absence of surface active substances the ONP prepeak height increases with time and with repeated scans.

According to some authors [10,13] this prepeak could be a reversible peak of redox couple of o-phenylhidroxylamine - o-nitrosophenol. According to Zuman and Fijalek [10] reduction of nitroso group occurs at the more positive potentials than that of the corresponding nitro group. McIntire at al. [13] reported that single, irreversible four electron wave of reduction of nitrobenzene possessed a prepeak upon scan reversal which represents the oxidation of phenylhidroxylamine to nitrosobenzene, which can be re-reduced back upon subsequent cathodic sweep.

ONP exhibits the prepeak at the mercury electrode both in the absence and in the presence of different adsorbed layers of organic substances at the electrode surface. The height of the prepeak could be significantly changed in the presence of adsorbed organic molecules on the mercury electrode. In the Figure 2 are presented changes of the normalized prepeak height of ONP in the presence of increasing concentrations of different surface active substances: fulvic acid and dextrane (Fig 2a) and humic acid and albumine (Fig 2c); the corresponding adsorption isotherms, which give us an information about degree of coverage of electrode surface are presented in Figs 2b and 2d.

(Figure 2)

From these Figures it is visible that the increase of the prepeak is closely connected with the formation of the adsorbed layers which are negatively charged at the used pH, i.e. in the case of fulvic and humic acids and albumine. What is worth to emphasize is that these effects are observed in the presence of very low concentrations of the mentioned model substances, which are also expected to be found in the natural water samples.

This suprising increase of prepeak height could possible be explained with enhancement of counter ions in such layers what lead to the enhancement of negatively charged ONP reduction product due to process of ion pairing. Similar phenomena is observed for the micelle enhanced ion pairing of the nitrobenzene radical anion in the anionic micelles [13].

For all cases the prepeak height is decreasing in the region where the electrode surface is completely covered with the organic molecules, and finally the prepeak completely disappears at the enough high concentrations of organic matter.

In the layer of dextrane which represents model for polysaccharide, and possesses no charge, there is no increase of ONP prepeak and there is even a small decrease of ONP prepeak height with increasing concentration of the dextrane (Figure 2a, curves 2A and

2B). The effects of the same concentrations of 0.6 mg l^{-1} of fulvic acid and dextrane are compared in Fig 3, a and b, respectively. The obvious difference in the prepeak height of ONP obtained in the presence of fulvic substance and polysaccharide could be a good basis for their differentiation in natural seawater samples and thus represents an improvement of ac voltammetric measurements using ONP probe.

(Figure 3)

2. Seawater samples

Rough estimation of the naturally present surface active substances in seawater samples is obtained on the basis of the comparison of electrochemical characteristics of the ONP voltammetric peaks obtained in the seawater sample with those obtained with the selected model organic substances, representative for the natural seawater samples (humic and fulvic acids, polysaccharide, lipids and proteins).

The proposed procedure for seawater samples consicts of several steps, as follows:

(i) The change of the ONP prepeak height at different accumulation times is used as a preliminary test of the type of organic material present in the sample, based on the developed model system;

(ii) The changes of the electrochemical characteristics of the main reduction peak of ONP (peak potential, peak current, peak shape) for different times of accumulation are used to confirm or discard the presence of supposed surface active substances.

(iii) Rough estimation of the concentration of dominant organic substances in the natural sample is obtained using calibration curves made by plotting of the peak potential and the normalized peak current of ONP main peak versus concentration of selected relevant model surface active substances.

(iv) The estimated concentrations are compared with the DOC values of the same samples and with the results of other more specific analysis, if they are available.

For the illustration of the validity of the described model system for the natural seawater samples voltammograms of six typical samples from the north Adriatic sea with added ONP are presented in the Figures 4a and b, 5a and b, and 6. In Table 1 are given DOC values, electrochemical characteristics of ONP peak, normalized peak current and peak potential, ONP prepeak heights, as well as the estimated values of the dominant type of organic matter in the samples investigated.

Seawater samples were taken from the north Adriatic sea which is a shallow basin rich in organic matter. This part of the Adriatic sea exhibits pronounced seasonal variations of organic matter as well as horizontal and vertical distribution related to the biological activity [14,15]. The concentrations of dissolved organic matter in the north Adriatic sea varied within range of 1-2 mg l^{-1} (83-166 μM C) with few exceptions. Looking at ONP prepeak height in the Figures 4a and b and Figures 5a and b it can be easily deduced that different type of material is adsorbed at the electrode surface in samples collected in different time periods. In the seawater samples from May dominant type of adsorbed material possesses negative charge resulting in a big increase of the ONP prepeak height. Prepeak heights for the samples collected in June are considerable lower.

<center>

(Table 1)

(Figure 4)

(Figure 5)

(Figure 6)

</center>

According to the big increase of the ONP prepeak height, and small shift of the potential of the main ONP peak it can be deduced that fulvic substances are dominant type of adsorbable organic material in the samples collected in May. With the prolonged time of accumulation, protein type of material is reaching the electrode surface, too (Figure 4a, curve 3). The shape of the ONP peak for very long accumulation time is most similar to the one obtained in the presence of model substance albumine, which represents a protein type of material. Owing to very big

increase of the prepeak height it is possible that humic type of material is also present in a smaller concentration, which does not influence the ac voltammetric characteristics of the main ONP reduction peak in these seawater samples. Concentrations of surface active substances were estimated using calibration curves for fulvic acid and albumine based on the effects of adsorbed surface active substances on the peak potential and peak height of ONP main peak at 180 s adsorption time.

For the sample taken at 0.5 m in May the observed peak potential corresponds to the value in the presence of either 1.5 mg l^{-1} of fulvic acid or 0.6 mg l^{-1} of albumine. From the decrease of the peak current we estimated the possible concentrations of about 2-3 mg l^{-1} of fulvic acid and 0.6 mg l^{-1} of albumine. Since the effects of protein and humic acid in the mixture with fulvic acid cause an overestimation of fulvic acid we have supposed that very probably the content of fulvic type of material in the particular sample is about 1 mg l^{-1}. The model mixture, which contained 1.0 mg l^{-1} of fulvic acid and 0.4 to 0.6 mg l^{-1} albumine showed very similar adsorption effects with the ONP probe as the natural seawater sample.

The same procedure was repeated with the sample taken at 30 m depth, only the estimated concentrations of 0.5 mg l^{-1} of fulvic acid and 0.4 mg l^{-1} of protein were lower in the sample taken at 0.5 m depth.

Seawater samples collected in June exhibited different ac voltammetric characteristics of the ONP probe. The characteristics of the prepeak and the main ONP peak, i.e. the peak shape, peak potential for the lower time of accumulation, indicate the presence of polysaccharide type of material in these samples. According to normalized peak height and peak potential the concentration of polysaccharide type of material is approx. 0.6 mg l^{-1} for the sample at 0.5 m and 0.4-0.5 mg l^{-1} for the sample at 30 m depth.

With prolonged accumulation time the type of organic matter adsorbed at the electrode is changing. As is shown in the Figure 6 (Station 107, 5 m, June 21, 1994) for a very long time of accumulation (curve 3) (70 minutes) the prepeak of the ONP is missing

where from one can conclude that the electrode surface becomes completely covered with organic molecules. The shape of the main ONP peak and its shift towards more negative potentials for long accumulation time indicate that humic type of material reached at the electrode surface. For the comparison with the model system ac voltammogram of the ONP in the presence of humic acid is given (Figure 6, curve 4). Here, it is important to notice that in solution of relatively high concentration of humic substance adsorption effect is obtained in a short time period.

The presence of humic substances in these seawater samples, in the mixture with polysaccharides is also indicated by their influence on the prepeak height for short time of adsorption. The relative increase of the prepeak height with depth is in accordance with the generally observed increased humic fraction in deeper layers [16]. Using calibration curves for the dependence of peak potential and normalized ONP peak height on concentration of HA for the 180 s of accumulation the concentrations of humic substances for the seawater samples collected in June, 1994 were estimated to be in the range between 0.4-0.6 mg l^{-1}.

As it is demonstrated for different model substances the ONP prepeak is very sensitive to the presence of different surface active substances. The effect depends both on the type and the concentration of the adsorbable material. The plot of normalized prepeak height versus concentration is very steep in the concentration range interesting for natural seawater samples. However, problems arise with analysis of natural samples because they contain complex mixture of various organic substances. For a more reliable quantitative estimation of present adsorbable organic solutes using ONP probe, especially on the basis of the prepeak measurement, it is necessary to study in more detail effects of model substances in mixtures of different composition. This will increase also our knowledge about competitive adsorption in mixtures and possible consequence for adsorption processes that occur at natural phase boundaries.

CONCLUSIONS

As natural water samples contain mixtures of different types of organic substances in very diluted solutions it is almost impossible to find out the method which enables complete insight to organic chemical composition of waters. The proposed electrochemical method using ONP as the probe is enough sensitive for rough characterization of the dominant type of adsorbable organic matter present in natural seawater samples. A great contribution to this method is selective sensitivity of ONP prepeak height to different organic substances adsorbed on the mercury electrode. For the negatively charged molecules increase of ONP prepeak height is observed. The extent of the increase and the concentration range of maximum effects are different for different organic layers. In the case of polysaccharides even slight decrease of ONP prepeak is observed.

In the combination with other methods such as for example fluorescence
[4], or another electrochemical method using Cd(II) as the probe [17,18] the approach using ONP probe seems promising for the better insight to the problems connected with the characterization of organic matter in natural waters.

On a number of seawater samples from north Adriatic sea it is demonstrated the application of developed method for the qualitative and quantitative characterization of organic composition of seawater. Obtained results are rough estimates which can serve as a good basis for more detailed analysis.

The estimated concentrations of the surface active organic substances are in a good agreement with the concentration range of DOC values for the investigated samples which is 0.98-1.7 mg l^{-1} (82-142 μM C).

REFERENCES

1. J.W. Farrington (Ed.) Marine Organic Geochemistry: Review and challenges for the future, Mar. Chem. 39 (1992) 242.

2. E.A. Romankevich, Geochemistry of Organic matter in the Ocean, Springer-Verlag, Berlin Heidelberg, 1984.

3. C. Lee and S. Wakeham, Chem. Oceanogr. 9 (1988) 1.

4. K. Mopper and C.A. Shultz, *Mar. Chem. 41* (1993) 229.

5. R.E. Baier, D.W. Goupil, S. Perlmutter and R. King, *J. Rech. Atmos. 8* (1974) 571.

6. K.A. Hunter and P.S. Liss: Organic Sea Surface Films, in *Marine Organic Chemistry,* E.K. Duursma and R. Dawson (Eds.). Elsevier, Amsterdam, 1982, pp. 259-298.

7. Bo`ena]osovi}: Aqueous Surface Chemistry: Assessment of Adsorption Characteristics of Organic Solutes by Electrochemical Methods, in *Chemical Processes in Lakes*, W. Stumm (Ed.). Wiley, New York, 1985, pp.55-88.

8. Bo`ena]osovi}: Adsorption Kinetics of the Complex Mixture of Organic Solutes at the Model and Natural Phase Boundaries, in *Aquatic Chemical Kinetics,* W. Stumm (Ed.). Wiley, New York, 1990, pp 291-310.

9. B. Ga{parovi} and B.]osovi}, *Mar. Chem. 46* (1994) 179.

10. P. Zuman and Z. Fijalek, *J. Electroanal. Chem. 296* (1990) 583.

11. A.M. Heras, J.L. Avila and F. Garcia-Blanco, *J. Electroanal. Chem. 170* (1984) 353.

12. R.P. Schwarzenbach, R. Stierly, B.R. Folsom and J. Zeyer, *Environ. Sci. Technol. 22* (1988) 83.

13. G.L. McIntire, D.M. Chiappardi, R.L. Casselbery and H. Blount, *J. Phys. Chem. 86* (1982) 2632.

14. B]osovi}, V. @uti}, V. Vojvodi} and T. Ple{e, *Mar. Chem. 17* (1985) 127.

15. J.C. Marty, V. @uti}, R. Precali, A. Saliot, B.]osovi}, N. Smodlaka and G. Cauwet, Mar. Chem. 25 (1988) 243.

16. V. Vojvodi} and B.]osovi}, Mar. Chem., submitted.

17. Z. Kozarac, B.]osovi} and V. Vojvodi}, *Wat. Res. 20* (1986) 295.

18. Z. Kozarac, M. Plav{i}, B.]osovi} and D. Vili~i}, *Mar. Chem. 28* (1989) 313.

Fig. 1.   Ac voltammograms (in phase) of 10^{-4} M ONP in 0.5 M NaCl, pH 8.4; first scan (curve 0), second scan at the same mercury drop, immediately recorded (curve A), and third scan at the same mercury drop, recorded after 30 s waiting at potential -0.35 V. Accumulation time 180 s.

The heights of peak (prepeak) are measured from the denoted base line.

Fig. 2.   (a and c) Dependence of the normalized current of the ac voltammograms of ONP prepeak (10^{-4} M) on the concentration of fulvic acid (curves 1A and 1B, 1A' and 1B'), dextrane (curves 2A and 2B), humic acid (curves 3A and 3B) and albumine (curves 4A and 4B).

A)   Second scan on the same mercury drop and B) third scan at the same mercury drop, recorded after 30 s waiting at the potential -0.35 V. Accumulation time 60 s (A and B) and 180 s (A' and B').

(b and d) Adsorption isotherms (surface coverage θ obtained from capacity current measurements vs. concentration of fulvic acid (1), dextrane (2), humic acid (3), and albumine (4). Accumulation time 60 s.

Fig. 3.   Ac voltammograms (in phase) of 10^{-4} M ONP in 0.5 M NaCl, pH 8.4; in the presence of 0.6 mg l^{-1} of a) fulvic acid and b) dextrane. Accumulation time 180 s. Curves (1) and (2) first scan, (A) second scan at the same mercury drop, immediately recorded and curve (B) third scan at the same mercury drop, recorded after 30 s waiting at the potential -0.35 V.

Fig. 4.   Ac voltammograms of 10^{-4} M ONP in seawater samples, (a) Station 101, 0.5 m, May 17, 1994, (b) Station 101, 30 m, May 17, 1994. Accumulation time (1) 0, (2) 180, and (3) 3 600 s. Curve (A) second scan at the same mercury

drop, immediately recorded, and (B) third scan at the same mercury drop, recorded after 30 s waiting at the potential -0.35 V.

Fig. 5. Ac voltammograms (in phase) of 10^{-4} M ONP in seawater samples: (a) Station 101, 0.5 m, June 21, 1994, (b) Station 101, 30 m, June 21, 1994. Accumulation time (1) 0, and (2) 180 s. Curve (A) second scan at the same mercury drop, immediately recorded, and curve (B) third scan at the same mercury drop, recorded after 30 s waiting at the potential -0.35 V.

Fig. 6. Ac voltammograms (in phase) of 10^{-4} M ONP in seawater sample, Station 107, 5 m, June 21, 1994 (1-3). Curve 4 is obtained in 0.5 M NaCl in the presence of 30 mg l^{-1} humic acid. Accumulation time (1) 0, (2) 180, (3) 4200, and (4) 60 s. Curve (A) second scan at the same mercury drop, immediately recorded, and curve (B) third scan at the same mercury drop, recorded after 30 s waiting at the potential -0.35 V.
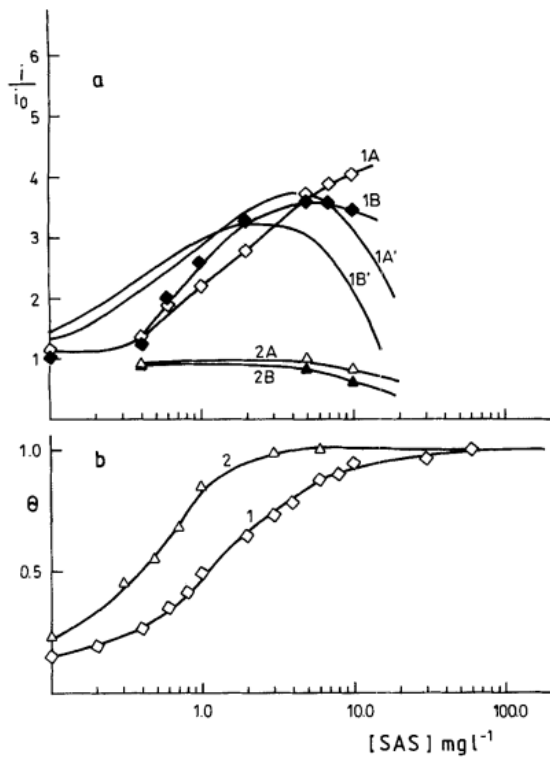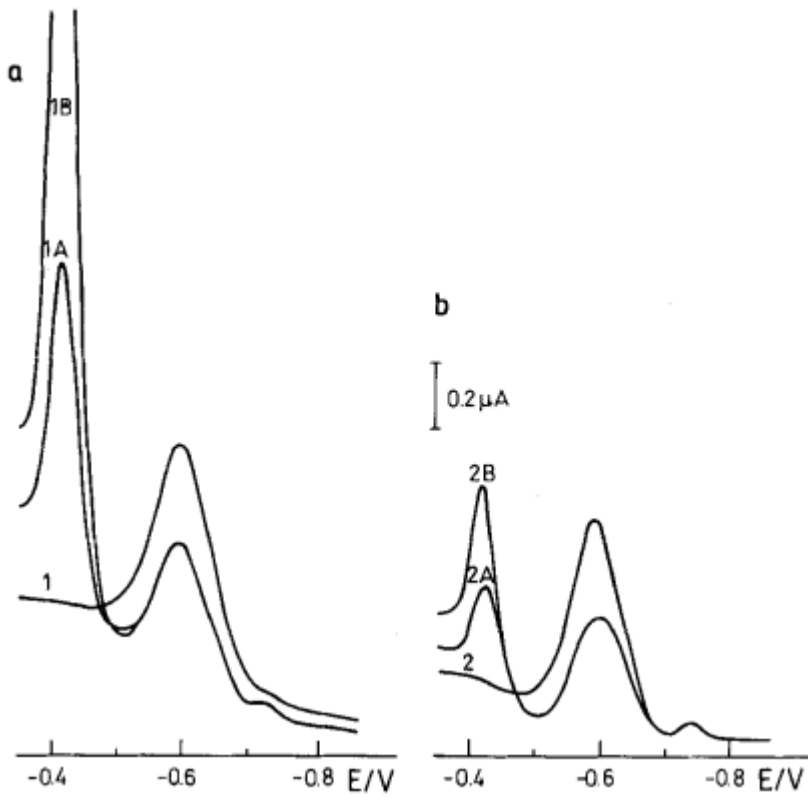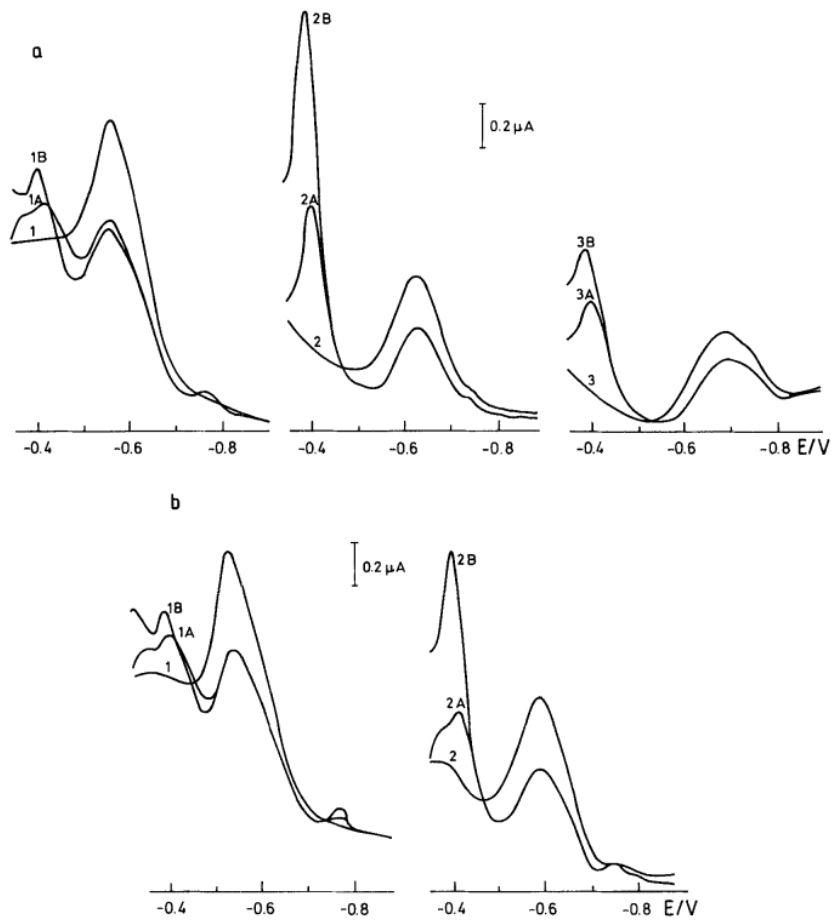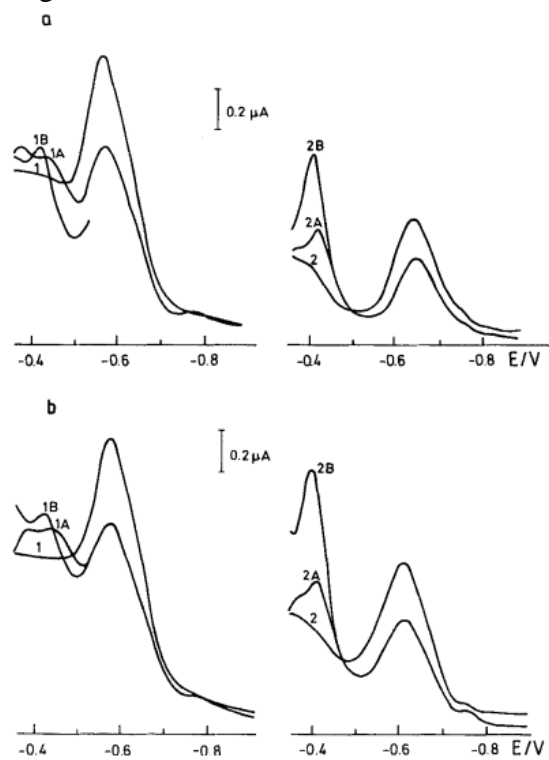
Fig. 1
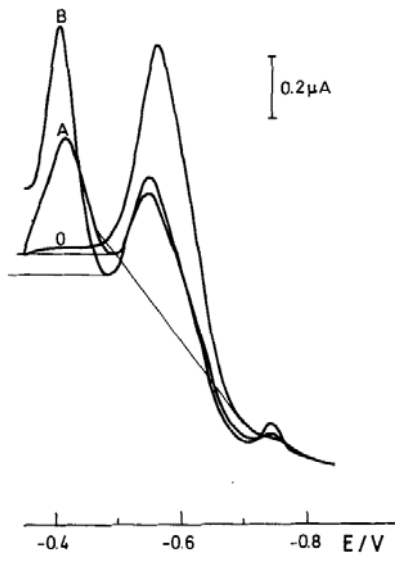
Fig. 2
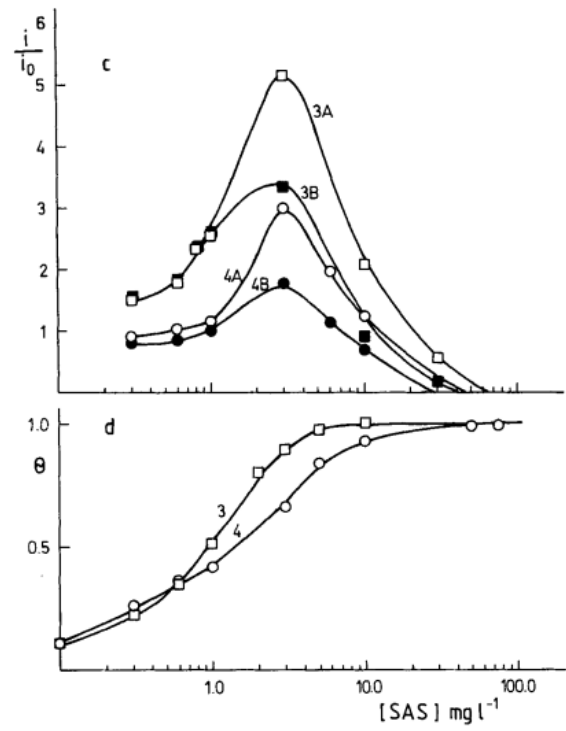
Fig. 3.

Fig. 4

Fig. 5.

Fig. 6.
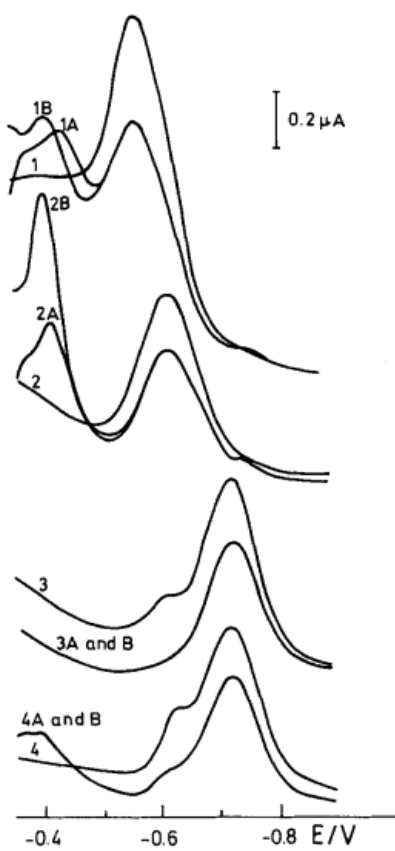
Table 1.   **Investigation of the seawater samples from the north Adriatic sea using ONP probe.**

DEPTH	DOC	i_p/i_{po} [a]	E_p/V [b]	i_A [c]		i_B [d]		ESTIMATED CONCENTRATIONS [e] (ng dm^{-3})			
		180 s	180 s	0 s	180 s	0 s	180 s	Fulvic acid	Humic acid	Polysacch aride	Protein e
Station 101, May 17, 1994	1.7	0.61	-0.63	2.36	7.96	4.78	16.30	~1.0			0.8
0.5	1.1	0.71	-0.59	2.90	5.3	4.52	11.64	0.5			0.4
30											
Station 101, June 21, 1994	1.3	0.58	-0.64	2.12	3.80	4.10	7.20		0.6	0.6	
0.5	1.0	0.66	-0.61	1.80	4.30	3.04	9.48		0.5	0.5	
30											
Station 107, June 21, 1994	1.04	0.68	-0.62	1.96	3.90	2.94	8.54		0.5	0.4-0.5	
5											

[a] i_p/i_{po}, normalized peak current of ONP; ipo is peak current in seawater without accumulation and i_p is peak current after accumulation of 180 s.

[b] E_p, peak potential of ONP reduction peak; -0.56 V in the absence of organic matter.

[c] i_A, prepeak current of ONP in seawater (second scan).

[d] i_B, prepeak current of ONP in seawater (third scan).

[e]   Estimated concentration of the dominant type of organic matter on the basis of analysis with ONP probe.